ISTANBUL TECHNICAL UNIVERSITY ★ INSTITUTE OF SCIENCE AND TECHNOLOGY

ACRYLONITRILE CONTAINING POLYMERS VIA COMBINATION OF ATOM TRANSFER AND NITROXIDE MEDIATED POLYMERIZATION

M.Sc. Thesis by

Özlenen Benian İLHANLI

Department : Polymer Science and Technology

Programme : Polymer Science and Technology

FEBRUARY 2006

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Date of submission : 19 December 2005

Date of defence examination: 31 January 2006

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FEBRUARY 2006

İSTANBUL TEKNİK ÜNİVERSİTESİ ★ FEN BİLİMLERİ ENSTİTÜSÜ

AKRİLONİTRİL İÇEREN POLİMERLERİN ATOM TRANSFER VE NİTROKSİT ORTAMLI POLİMERİZASYONU

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Tezin Enstitüye Verildiği Tarih : 19 Aralık 2005

Tezin Savunulduğu Tarih : 31 Ocak 2006

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ŞUBAT 2006

ACKNOWLEDGEMENT

This master study has been carried out at Istanbul Technical University, Chemistry Department of the Science and Letter Faculty.

First I would like to express my gratitude to my advisor Prof. Dr. Ümit Tunca and co-supervisor Prof. Dr. Gürkan Hızal for offering invaluable help in all possible ways, continuous encouragement and helpful critisms throughout this research.

I would like to thank to my colleagues Aydan Dağ, Bige Tuğçe Çolakoğlu, Eda Güngör, Figen Karataş, Özcan Altıntaş, Hakan Durmaz and Hümeyra Mert who supported me from the beginning of my master study, and and encouragement during my laboratory works.

I also would like to thank to Tuba Erdoğan Bedri who shared her knowledge and experience with me and for her constructive comments.

Finally, I would like to offer the most gratitude my parents Turan İLHANLI and Hayret İLHANLI for their patience, understanding and support during all stages in the preparation of this thesis.

February 2006 Özlenen Benian İLHANLI

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LIST of SYMBOLS

M_n	**:** Number average molecular weight of polymers
M_w	**:** Weight average molecular weight of polymers
MWD	**:** Molecular weight distribution of polymers
PnBA	**:** Poly (n-butylacrylate)
PAN	**:** Poly (acrylonitrile)
PS	**:** Polystyrene
SAN	**:**Styrene/Acrylonitrile
Cat	**:** Catalyst
k_a, k_d	**:** Rate constants of activation and deactivation steps of the initiation in radical polymerization
K_{eq},k_p	**:** Equilibrium rate constant and rate constant of propagation step in radical polymerization respectively
k_{tc}, k_{td}	**:** Rate constant of termination by combination and rate constant of termination by disproportionation respectively
EtOH	**:** Ethanol
Et_3N	**:** Triethylamine
I, M	**:** Initiator and monomer respectively
Ph	**:** Phenyl

ACRYLONITRILE CONTAINING POLYMERS VIA COMBINATION OF ATOM TRANSFER AND NITROXIDE MEDIATED POLYMERIZATION

SUMMARY

Accurate control of polymerization processes to give polymers with well-defined architecture is becoming an increasingly important aspect of polymer chemistry. The field of radical polymerization has exploded with the advent of controlled radical polymerization processes. Radical polymerization is a very important commercial process for preparing high molecular weight polymers. The only disadvantage of conventional radical polymerization is the poor control of macromolecular structures including end functionalities and polydispersities due to chain transfer and termination processes. Specifically, controlled architecture possesses some characteristics, which are molecular weight control, end group control, ability to form block copolymers, and a living nature. Recently, the controlled/'living' radical polymerizations have been utilized for the synthesis of well-defined, narrow polydispersity polymers. Among them nitroxide mediated polymerization (NMP) and copper catalyst mediated atom transfer radical polymerization (ATRP) are versatile methods for the controlled radical polymerization of various monomers. NMP is based on the use of stable nitroxide free radicals, such as 2,2,6,6-tetrametylpiperydinyl-1-oxy (TEMPO), as thermally labile capping agents for the growing polymer chain, which leads to control of the polymerization. In 1995, Matyjaszevski et al. developed an alternative controlled/'living' free radical polymerization process using a copper (I)- catalyzed system. Atom transfer radical polymerization (ATRP) is a convenient method especially for the preparation of polymers and block copolymers because the 2-bromopropionate group, which is an efficient initiator of ATRP, can easily be introduced as the end group to different polymers.

One of the advantageous of controlled radical polymerizations such as NMP and ATRP is that the molecular weight and the chain end functionality can be controlled. The wide range of functionality can be introduced into a polymer chain end using asymmetric difunctional initiator if one of the functional group remains intact during the polymerization. This has enabled the synthesis of well-defined block copolymers by a sequential two-step or one pot method without any transformation or protection of initiating sites.

In the present work, novel asymmetric double functional initiator, 2-phenyl-2-[(2,2,6,6-tetramethylpiperidino) oxy] ethyl 2-bromopropanoate was synthesized and we used difunctional initiator for the synthesis of well-defined SAN copolymers, polystyrene-*block*-polyacrylonitrile (PS-*b*-PAN), polystyrene-*b*-poly(*n*-butyl acrylate)-polyacrylonitrile (PS-*b*-PBA-*b*-PAN) and also block copolymers containing random SAN sequences and styrene by the combination of ATRP and NMP processes. ^{1}H-NMR (Nuclear Magnetic Resonance), GPC (Gel Permeation Chromatography), IR (Infrared Spectrum) and DSC (Differential Scanning

Calorimeter) studies of the obtained polymers show that block copolymers are readily formed as a result of combination of ATRP and NMP mechanisms.

AKRİLONİTRİL İÇEREN POLİMERLERİN ATOM TRANSFER VE NİTROKSİT ORTAMLI POLİMERİZASYONU

ÖZET

İyi tanımlanmış mimariye sahip polimerlerin tam kontrollü polimerizasyon yöntemleriyle eldesi polimer kimyasında gittikçe artan bir öneme sahiptir. Radikal polimerizasyon alanı kontrollü radikal polimerizasyon yöntemlerinin keşfiyle büyük bir patlama yapmıştır. Radikal polimerizasyonu yüksek molekül ağılıklı polimerlerin eldesinde kullanılan çok önemli ticari bir yöntemdir. Klasik radikal polimerizasyonun tek dezavantajı zincir transfer ve sonlanma reaksiyonlarından dolayı makromolekülün yapısıyla birlikte fonksiyonalitesi ve polidispersitesi üzerinde düşük bir kontrole sahip olmasıdır. Kontrollü mimari denilince, molekül ağırlık kontrolü, uç grup kontrolü, blok kopolimer oluşturabilme ve yaşayan karakter akla gelmektedir. Son yıllarda, iyi tanımlanmış düşük polidispersiteye sahip polimerlerin sentezinde kontrollü/'yaşayan' polimerizasyon yöntemleri kullanılmaktadır. Bu yöntemler içinde en etkili olanı nitroksit ortamlı polimerizasyonu (NMP) ve Cu(I) kataliz sistemli atom transfer radikal polimerizayonudur (ATRP). Nitroksit ortamlı polimerizasyon (NMP) kararlı serbest nitroksit radikalinin, 2,2,6,6-tetrametilpiperidinil-1-oksi (TEMPO), kullanımına dayanmaktadır ve bu sistemde TEMPO büyüyen zincirin sonunda ısısal olarak kopabilen bir uç grup olarak kontrollü polimerizasyona neden olmaktadır. Matyjaszewski ve grubu 1995 yılında Cu (I) kataliz sistemi kulanılan alternatif bir kontrollü/'yaşayan' polimerizasyon yöntemi geliştirmişlerdir. Atom transfer radikal polimerizasyonu (ATRP), özellikle blok kopolimerlerin eldesinde kullanılan çok yaygın ve uygun bir metotdur, çünkü ATRP için çok etkili bir başlatıcı olan 2-bromo propanoat farklı polimerlerin uç gruplarına kolaylıkla yerleştirilebilmektedir.

NMP ve ATRP gibi kontrollü polimerizasyon tekniklerinin bir avantajı da elde edilen polimerlerin molekül ağırlıklarının ve zincir uç grubu fonksiyonalitesinin kontrol edilebilir olmasıdır. İki fonksiyonlu asimetrik başlatıcılar kullanılarak polimer zincir uç gruplarına çok çeşitli fonksiyonellikler kazandırılabilir ki bu da herhangi bir transformasyon reaksiyonu gerektirmeden düşük molekül ağırlık dağılımına ve kontrollü molekül ağırlıklarına sahip polimerlerin eldesine olanak tanır.

Bu çalışmada, iki fonksiyonlu asimetrik başlatıcı, 2-fenil-2-[(2,2,6,6-tetrametilpiperidinil)oksi]etil 2-bromo propanoat sentezlenmiş ve ATRP ve NMP yöntemleri kullanılarak SAN kopolimerler, polystyrene-block-polyacrylonitrile (PS-*b*-PAN), polystyrene-*b*-poly(n-butyl acrylate)-polyacrylonitrile (PS-*b*-PBA-*b*-PAN) and ayrıca styrene ve düzensiz SAN segmentlerini içeren blok kopolimerleri sentezlenmiştir. ^{1}H-NMR(Nükleer Manyetik Rezonans Spektroskopisi), GPC(Jel Geçirgenlik Kromatografisi), IR(Infrared Spektroskopisi) ve DSC(Diferansiyel Taramalı Kalorimetri) cihazlarından alınan sonuçlar doğrultusunda elde edilen blok

kopolimerlerin gerçekten de ATRP ve NMP tekniklerinin kombinasyonu ile oluştukları belirlenmiştir.

1. INTRODUCTION

Polyacrylonitrile (PAN) is an industrially important polymer due to its well-known characteristics including good resistance to solvents, high rigidity, low gas permeability and exceptional barrier properties to oxygen and carbon dioxide. Since PAN decomposes before reaching its melting temperature of about 300 ^{o}C, it could not be used as a plastic. However, the copolymers of acrylonitrile (AN) with other monomers are widely used to enhance the solution processability and economical attractive melt processing [1, 2]. Styrene-acrylonitrile copolymers (SAN) are widely used in packaging materials, house wares and custom-molding products. Moreover, the copolymers of AN and alkyl acrylates combine superior mechanical properties. The synthesis of PAN and its related copolymers are typically carried out via conventional free radical polymerization which fails of control over molecular weight and structure [3]. The advent of controlled radical polymerization (CRP) leads to synthesize of polymers with controlled molecular weight and well-defined architecture. Copper catalyst-mediated atom transfer radical polymerization (ATRP) [4-6] and nitroxide mediated polymerization (NMP) [7, 8] are versatile methods for CRP of vinylic-type monomers. Synthesis of SAN and its related block copolymers via ATRP have been reported by Matyjaszewski et al [9]. NMP also permits the preparation of SAN in a control manner [10]. On the other hand, the preparation of PAN by ATRP with a detailed kinetic study was first reported by Matyjaszewski and co-workers [11, 12]. The synthesis of block copolymers containing PAN blocks exhibits some difficulties due to the limited solubility of PAN blocks in common solvents used in CRP. In point of fact, there have been a few studies on the preparation of block copolymers containing pure PAN segments in the backbone. Matyjaszewski et al reported the synthesis of polyacrylonitrile-*block*-poly (n-butyl acrylate), (PAN-*b*-PBA) using ATRP and NMP however the best results were observed by ATRP [13]. Recently, the synthesis of polyacrylonitrile-*block*-polystyrene (PAN-*b*-PS) copolymers was reported by chain extension of PAN macroinitiator through ATRP [14, 15].

In the light of these considerations, we established a versatile route to the preparation of PAN containing block copolymers using a difunctional initiator combining initiator sites for both NMP and ATRP. In our previous research, we reported the synthesis of novel asymmetric difunctional initiators containing 2,2,6,6-tetramethylpiperidinyl-1-oxy (TEMPO) and 2-bromo propanoate or 2-bromo-2-methyl propanoate groups as well as their use as initiators in the preparation of di- and tri- block copolymers (containing styrene (St), methyl methacrylate (MMA) and tert-butyl acrylate (tBA) segments) via combination of ATRP-NMP, ATRP-ATRP-NMP and vice versa [16, 17]. In this study, we used difunctional initiator for the synthesis of well-defined SAN copolymers, polystyrene-block-polyacrylonitrile (PS-*b*-PAN), polystyrene-*b*-poly (n-butyl acrylate) (PS-*b*-PBA-*b*-PAN) and also block copolymers containing random SAN sequences and styrene by the combination of ATRP and NMP processes.

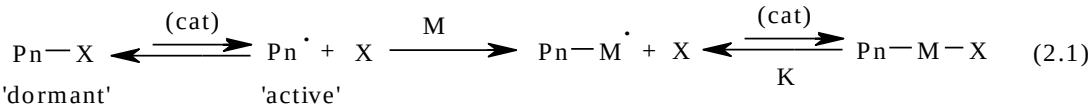
2. THEORETICAL PART

2.1. Controlled or 'Living' Free-Radical Polymerization

From the foregoing section one can deduce that ideally the versatility of free radical polymerization and the control over molecular weight, chemical composition and chain architecture, like in an anionic polymerization, are being combined in a single process. The last decade several of such techniques that combine the advantages of free-radical polymerization and those of living polymerizations were invented [18]. These processes are being referred to as controlled or 'living' free radical polymerizations and are based on two principles: reversible termination or reversible transfer. Examples of processes that rely on reversible termination are nitroxide mediated polymerization (NMP) [19] and atom transfer radical polymerization (ATRP) [4]. In these processes species are added which prevent bimolecular termination by reversible coupling. In NMP this species is a nitroxide, whereas in ATRP this species is a halide atom, originating from a introduction transition-metal complex to which it can be transferred reversibly. Processes that are based on reversible transfer include degenerative transfer (DT) [20] and reversible addition-fragmentation chain transfer (RAFT) [21]. In these processes there is a fast exchange between growing radicals and dormant species via transfer reactions, during which the RAFT-moiety (dithioester) or the DT-moiety (iodine atom) and radical activity are being exchanged. In RAFT this exchange proceeds via an intermediate radical, whereas in DT there is a direct exchange. In order to extend the lifetime of the propagating chains, each of these methods relies on establishing a dynamic equilibrium between a low concentration of active propagating chains and a predominant amount of dormant chains that are unable to propagate or terminate. In the case of NMP or ATRP, the equilibrium is pushed to the left-hand side (deactivated, k_{deact}), forming an excess of dormant species as a result of the persistent radical effect [22]. In all radical polymerizations, biradical termination occurs at a rate, Rt, which is dependent on the concentration of radicals, [P*], where Rt= kt [P*] [23]. Therefore, at the same polymerization rate (the same [P*]), essentially the same

number of chains terminate regardless of being in conventional or CRP systems. However, in the conventional process all chains are terminated, whereas in CRP, as a result of the greater number of growing chains, the terminated chains constitute a small fraction of all the chains (~1-10%). The remaining chains are dormant species, capable of reactivation, functionalization, and chain extension to form block copolymers, etc. Thus, CRP behaves as a 'living' system [24, 25]. Additionally, relatively fast initiation, at least as fast as propagation, gives control over molecular weight (the degree of polymerization is defined by the ratio of concentrations of the consumed monomer to the introduced initiator, $DP_n = [M]_0/[I]_0$ and a narrow molecular weight distribution. CRP may be used to form new (co)polymers, including, for example, gradient [26], block [27], tri- and multi-arm star copolymers[28], site-specific functional polymers [29], and graft copolymers with controlled graft density and graft distribution [30, 31]. The capabilities of CRP differ from earlier ionic living polymerization processes as a result of the adaptability of radical polymerization processes to different polymerization systems and the tolerance of CRP to functional groups on the monomer unit. CRP can be run in the presence of water [32], ionic liquids [33, 34], and supercritical CO_2 [35]. CRP processes have been developed for biphasic [32, 36, 37] and homogeneous aqueous media [38, 39], and for the direct polymerization of acidic, basic, and ionic monomers to form homopolymers [40, 41] and block copolymers [42, 43].

The latest developments in living free radical polymerizations of vinyl and cyclic monomers are base on the reversible protection of the growing chains in the form of inactive 'dormant' species exchanging reversibly with the active growing chain as seen in (2.1).



(2.1)

Cat = Nu^-, Lewis acids, hv, heat, X= Protective group

P_n = Polymer chain, M = Monomer, K = Equilibrium constant

Controlled polymerization requires a low proportion of deactivated chains, which can be achieved by keeping molecular weight sufficiently low. This necessitates a relatively high concentration of the initiator, or in other words, low $[M]_0 / [I]_0$ ratios. However when $[I]_0$ is high, since the termination is bi-molecular, contribution of

termination becomes more significant when a large concentration of radicals [P.] is generated.

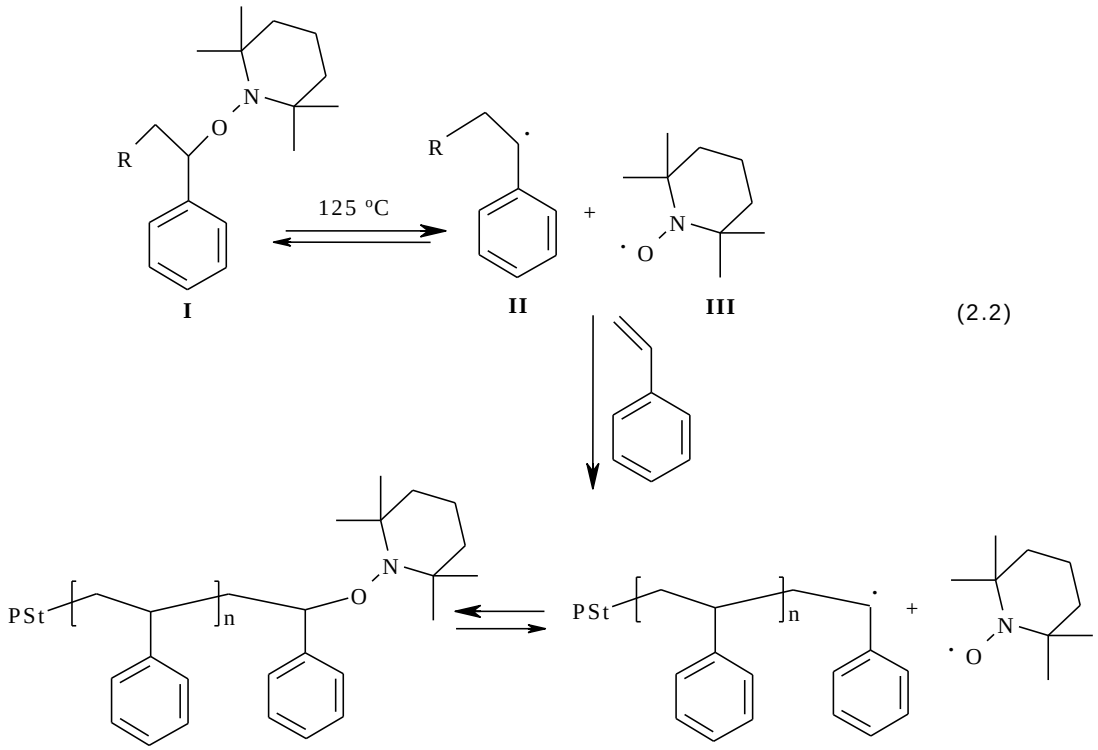
Therefore establishing an exchange between dormant and active species is necessary to solve this discrepancy. The concentration of dormant species can be equal to $[I]_0$, and the concentration of momentarily growing species to [P.]. The total number of growing chains will be equal to $[I]_0$, and radicals would be present at a very low stationary concentration, [P.], and therefore the contribution of termination should be very low. There are three possibilities to realize the concept of controlled radical polymerization.

2.1.1. Nitroxide-mediated polymerization

Nitroxide-mediated polymerization (NMP) represents one of the most advantageous methods for synthesizing tailor-made macromolecular architectures [44, 45]. In this type of CRP, alkoxyamine initiators and nitroxide persistent radicals have been effectively used to polymerize styrenes and acrylates. In certain systems, alkoxyamines have also been generated in situ by the initial use of conventional radical initiators (AIBN and peroxides) and nitroxide persistent radicals, which also led to a CRP process [46]. A widely used nitroxide in the polymerization of styrene (Sty) is 2,2,6,6-tetramethylpiperidinyloxy (TEMPO), although recently developed nitroxides can also polymerize acrylates in a controlled fashion [47, 48] The current limitation in this system lies in the inability to successfully polymerize methacrylate monomers, because of, -hydrogen elimination to the nitroxide radicals. Additionally, thiuram disulfides and dithiocarbamate “iniferter” systems have been used as agents for CRP with limited success [49].

2.1.1.1. Mechanism of nitroxide-mediated polymerization

The mechanism of nitroxide-mediated polymerization is based on the reversible activation of dormant polymer chains (Pn-T) shown in Scheme 2.2. This additional reaction step in the free-radical polymerization provides the living character and controls the molecular weight distribution. The schematic representation of the mechanism of NMP is given in (2.2)



(2.2)

When a dormant species or alkoxyamine dissociates homolytically, a carbon centered radical and a stable nitroxide radical are formed in (2.2). This is a reversible process and the reversible reaction is close to diffusion control, but at high enough temperatures where dissociation is competitive, the polymeric radicals (Pn·) can add to monomer, which allows step wise growth of the polymer chains. The nitroxide is an ideal candidate for this process since it only reacts with carbon-centered radicals, is stable and does not dimerize, and in general couples nonspecifically with all types of carbon centered radicals (close to diffusion controlled rates).

In an ideal NMP, polymerization is started using an alkoxyamine as initiator such that no other reactions than reversible activation of dormant species and addition of monomer to carbon-centered radicals take place. The alkoxyamine consist of a small radical species, capable of reacting with monomer, trapped by a nitroxide. Upon decomposition of the alkoyamine in the presence of monomer, polymeric dormant species will form and grow in chain length over time. However, this is not a clean reaction and side products can form. Since the nitroxide and the carbon-centered radical diffuse away from each other, termination by combination or disproportionation of two carbon centered radicals cannot be excluded. This will lead to the formation of 'dead' polymer chains and an excess of free nitroxide. The built-up of free nitroxide is referred to as the persistent radical effect [22] and slows down the polymerization, since it will favor trapping (radical-radical coupling) over

propagation. Besides termination, other side reactions play an important role in nitroxide-mediated polymerization. One of the important side reactions is decomposition of dormant chains [50], yielding polymer chains with an unsaturated end-group and a hydroxyamine, TH. Another side reaction is thermal self-initiation [51], which is observed in styrene polymerizations at high temperatures. Here two styrene monomers can form a dimer, which after reaction with another styrene monomer, results in the formation of 2 radicals. This additional radical flux can make up the loss of radicals due to irreversible termination and allows the polymerization to proceed successfully, providing that the number of initiating radicals is small compared to the number of nitroxide-trapped polymer chains [9]. Also systems that do not show thermal self-initiation can be set under control by use of an additional initiator, which will provide the additional radical flux [9]. In addition, the dimer formed can react with a nitroxide molecule to provide the dimer radical and a hydroxyamine. Although NMP is one of the simplest methods of living free radical polymerization (LFRP), it has many disadvantages.

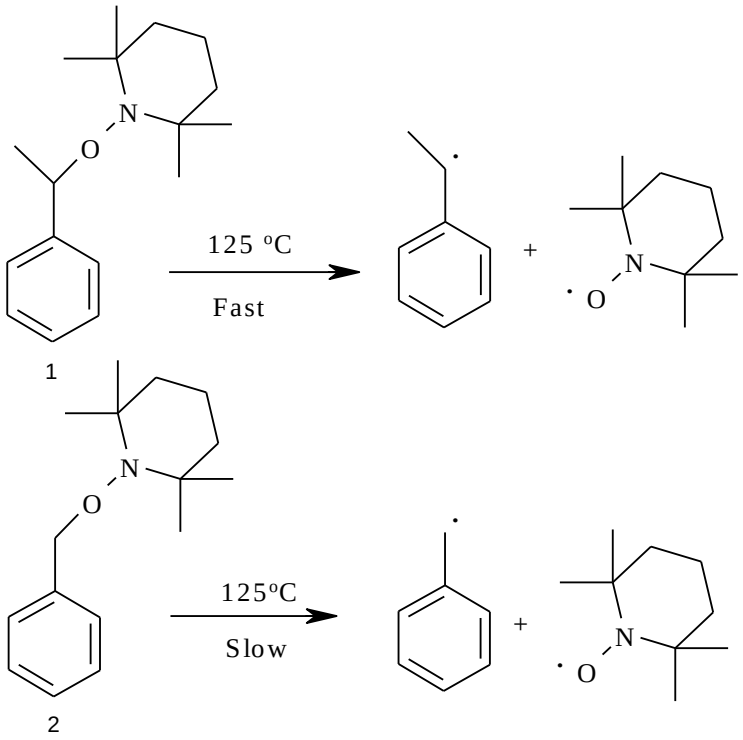
Many monomers will not polymerize because of the stability of the dormant alkoxyamine that forms. Also, since the reaction is kinetically slow, high temperatures and bulk solutions are often required. Also, the alkoxyamine end groups are difficult to transform and require radical chemistry. The most popular nitroxide used for NMP in the past has been TEMPO. However, TEMPO is limited in the range of monomers which are compatible to polymerize by NMP, mostly due to the stability of the radical. Hawker et. al. recently discovered that by replacing the α-tertiary carbon atom with a secondary carbon atom, the stability of the nitroxide radical decreased which lead to an increased effectiveness in polymerization for many monomers in which TEMPO was uneffective [47]. While TEMPO and TEMPO derivatives are only useful for styrene polymerizations, the new derivatives permit the polymerization of acrylates, acrylamides, 1, 3-dienes, and acrylonitrile based monomers with very accurate control of molecular weights and low polydispersities. The chain end functionalization of polymers synthesized by NMP is a significant problem because dormant chains containing alkoxyamines can regenerate terminal radicals which can depolymerize at high temperatures. A very interesting chain end functionalization process has also been discovered by Hawker et. al. which involves the controlled monoaddtion of maleic anhydride or maleimide

derivatives to the alkoxyamine chain end [52]. The alkoxyamine can then be easily eliminated and other functional groups can be introduced. This process relies on the resistance of maleic anhydride or maleimide derivatives to homopolymerize and the ability of the precurser to reform the olefin by elimination of the hydroxylamine. NMP is an excellent method for synthesizing diverse and well defined macromoloecular structures. Block copolymers can be synthesized in many varying ways.

2.1.1.2. Mechanical considerations

The alkoxyamine type of initiators, which on decomposition, gives an initiating benzylic radical and a nitroxide radical in the desired 1:1 stoichiometry. It has recently been shown that the strength of the C-ON bond in alkoxyamine-based initiator is of crucial importance to the success of living free radical polymerization. If C-ON bond is too thermally stable then the homolysis is slow compared to the propagation, leading to uncontrolled polymerizations.

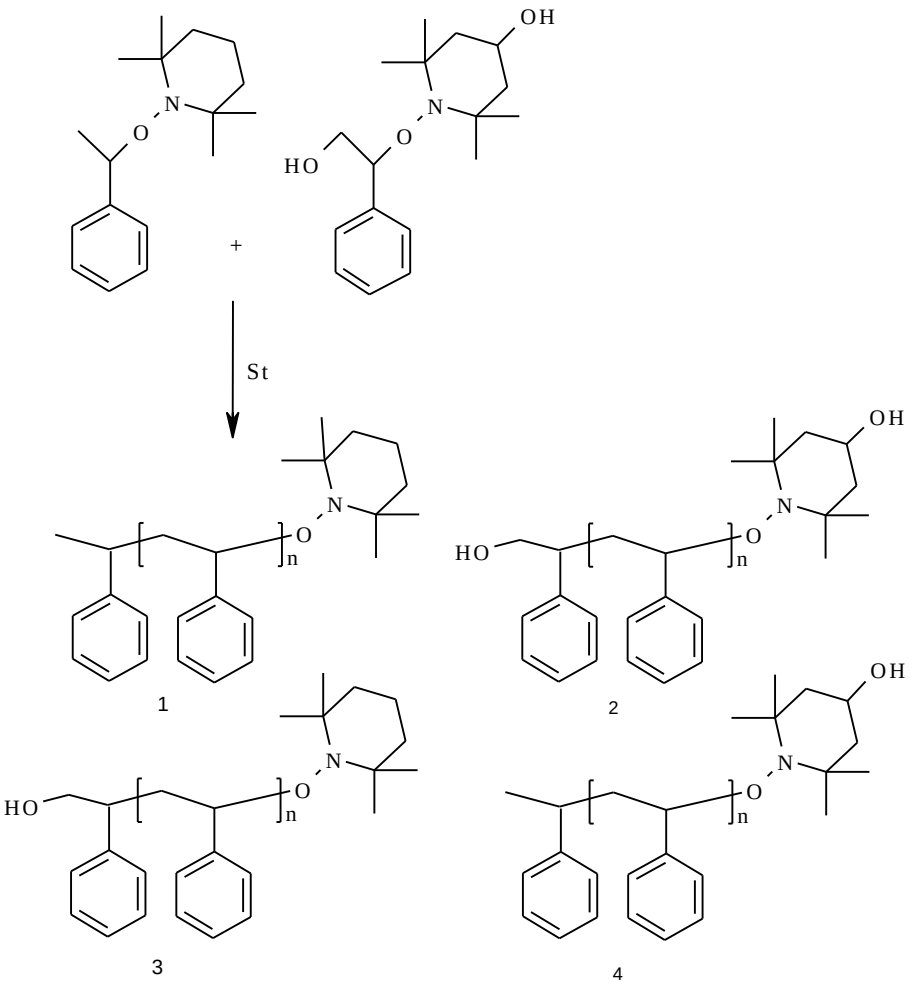
It was found that a variety of functional groups could be substituted on the aromatic ring, nitroxide unit or α-carbon without affecting the polymerization process deleteriously. However if the α-methyl group is removed to give parent benzyl-TEMPO derivative, as seen in (2.3) as (2), a substantial loss of control over the polymerization is observed in the study of Malmstrom and Hawker. The reasons for this dramatic change are shown in the same work as the difference in stability, or rate of formation, for the initiating benzylic radical.



(2.3)

The steric or electronic nature of nitroxide can significantly increase the rate of polymerization [53]. For example Puts and Sogah [54] have shown that by replacement of two methyl groups with phenyl groups to give 2,5-dimethyl-2,5-diphenylpyrolidine-1-oxyl, instead of TEMPO, a significant increase in the reaction rates is observed, which allows the polymerization to be conducted at lower temperatures.

The propagation step in nitroxide living free radical polymerization may either occur via an associative, or insertion type, mechanism or by dissociative mechanism, in which the nitroxide completely dissociates from the growing polymer chain end. To determine which of these are operating, Malmstrom and Hawker conducted series of experiments in the standard living polymerization conditions and in the presence of two similar initiators, which differ from each other in the presence of, or absence of hydroxyl groups. Theoretically if an insertion type occurs only two products should be formed, seen in (2.4) as (1) and (2). However, nitroxide is free to diffuse into polymerization medium and undergoes exchange with other propagating chain ends and so as a result, (3) and (4) types of products could also be obtained.



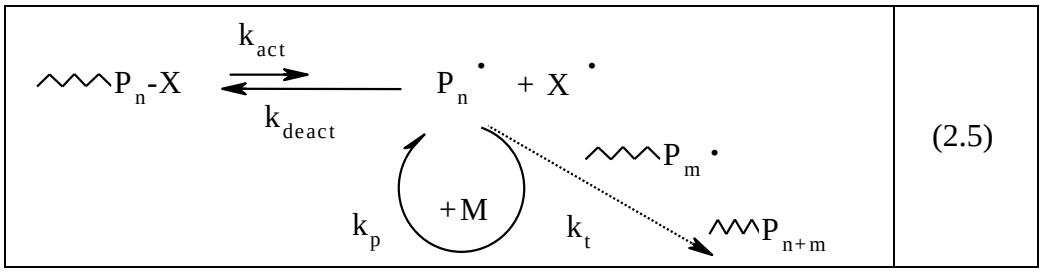
(2.4)

Since the stable free radical polymerizations are conducted at relatively high temperatures, auto-polymerization should not be ignored. To gain a better understanding of auto-polymerization a series of experiments, in which styrene was heated at 125°C in the absence of initiator, but in the presence of a nitroxy radical, TEMPO. At the end of the experiments polymers having low polydispersities and molecular weights that corresponded to the theoretically calculated ones were obtained. This shows that unexpectedly high degree of control occurred meaning that chains are being initiated by auto-polymerization, with the role of nitroxide being to control the polymerization. The radicals are slowly formed during the polymerization. The radicals formed by self-initiation are initially trapped by the scavengers and then when the concentration of the scavengers is low enough and the concentration of the growing radicals is high enough polymerization starts. This is evidenced by long induction period. As a result, according to Matyjaszevski it is not necessary to use radical initiators in NMP of styrene.

2.1.2. Atom transfer radical polymerization (ATRP)

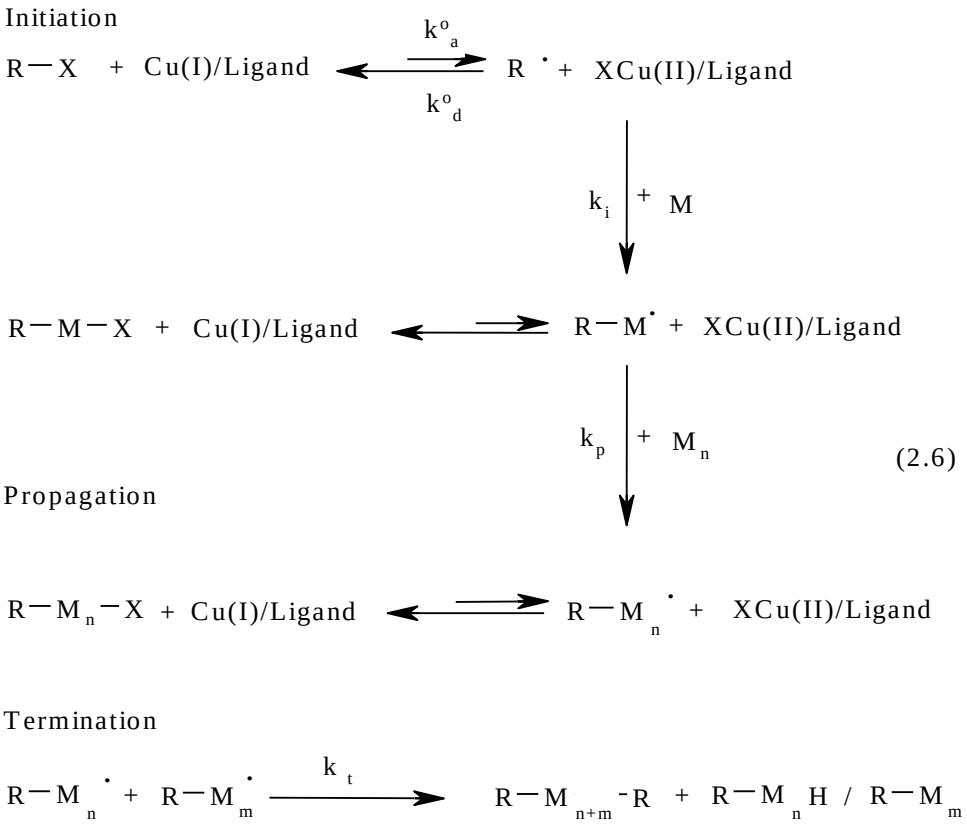
Synthesis of polymers with well-controlled architecture and predictable molecular weight is currently of great academic and industrial interests [55,29], while atom transfer radical polymerization (ATRP) is one of the relatively new and versatile methods for controlled polymerizations [4,56]. Initiator is of prime importance for an ATRP. The reason is twofold. One is that the main role of the initiator is to determine α-end-function of polymers [57,58]. Various functionalized polymers with large conjugated function at α-end can be obtained using different initiators. The other is that different initiating systems have different initiation activities which directly affect the polymerization rate and temperature [56,59]. Although the monomers of methacrylate can be polymerized in many ATRP systems even at ambient temperature [56,59], it is still uncommon for polymerization of styrene to be reached at such room temperature [56,59].

The control over radical polymerizations is based on two principles. First, initiation should be fast, providing a constant concentration of growing polymer chains. Secondly, because of the persistent radical effect [22], the majority of these growing polymer chains are dormant species that still preserve the ability to grow because a dynamic equilibrium between dormant species and growing radicals is established. By keeping the concentration of active species or propagating radicals sufficiently low throughout the polymerization, termination is suppressed. ATRP is a radical process that fulfills these requirements by using a transition metal, in combination with a suitable ligand. The catalyst complex establishes a reversible equilibrium between growing radicals and dormant species (the proposed mechanism for ATRP is given in 2.5). The equilibrium is attenuated by the choice of the ligand and the ligand also increases the solubility of the catalyst complex in the polymerization medium. Additionally, when the concentration of propagating radicals is sufficiently low in comparison with dormant chains, the proportion of terminated chains, P_{m+e} can be often neglected (<5%). This may enable the preparation of highly functional polymers (>95%).



(2.5)

The schematic representation of the mechanism of ATRP is given in (2.6)



(2.6)

In homogeneous systems, the rate of ATRP has been shown to be first order with respect to the monomer and initiator. The rate of the polymerization is also influenced by the ratio of concentrations of the activator to deactivator, although this may change during polymerization.

$$R_p = k_{app} [M] = k_p [P.][M] = k_p K_{eq} [I]_0 \ [Cu (I)]/ [Cu (II) X] \times [M] \qquad (2.7)$$

The opportunity to incorporate a functional end group in a linear polymer chain is available by varying the initiator, i.e. a low molecular weight organic compound RX, containing an activated halogen X. After initiation has occurred, the initiator fragment R is present at one end of the chain while the halogen at the other end can be futher transformed to various functionalities by means of standard organic

procedures. Moreover, because of the radical nature of ATRP, a wide range of functional monomers can be polymerized yielding polymers with pendant groups. The produced polymer can further be used to obtain block copolymers because of the 'livingness' of the radical process [4].

ATRP is also a robust synthetic tool for the preparation of well-defined functional polymers and polymers of various pre-selectable architectures. A variety of functional polymers with backbone or terminal-group functionalities such as hydroxyl, carboxylic acid, amino, macromonomers (allyl, vinyl) and side chain liquid crystalline polymers have been synthesized in a well-controlled manner. ATRP has been used to construct polymer architectures including block copolymers, star, polymer brushes, comb-like polymers, dendrimer-like star-block copolymers and hyperbranched polymers, as well as very complex structures, organic/ inorganic hybrid nanomaterials, just to name a few examples. Therefore, ATRP represents one of the most versatile synthetic tools for the preparation of new polymer materials [60].

One of the most important parameters in ATRP is the dynamics of exchange, and especially the relative rate of deactivation. If the deactivation process is slow in comparison with propagation, then a classic redox initiation process operates leading to conventional, and not controlled, radical polymerization. Polydispersities in ATRP decrease with conversion, with the rate constant of deactivation, k_d, and also with the concentration of deactivator, [XCu(II)].They, however, increase with the propagation rate constant, k_p, and the concentration of initiator, $[RX]_0$. This means that more uniform polymers are obtained at higher conversions, when the concentration of deactivator in solutions is high and the concentration of initiator is low. Also, more uniform polymers are formed when deactivator is very reactive (e.g. copper(II) complexed by 2,2'-bipyridine or pentamethyldietylenetriamine rather than by water) and monomer propagates slowly (styrene rather than acrylate).

2.1.2.1. Initiators

In ATRP, initiation is accomplished through homolytic cleavage of activated halogen-containing compounds and addition of the generated radicals to alkenes. The radical-stabilizing group should reside on the R-C atom (aryl, carbonyl, nitrile, multiple halogens) or involve weak bonding with heteroatoms (S, N, O). Direct

bonding of the halogen to an aryl or carbonyl group does not facilitate radical generation, and since vinyl, acyl halides, or haloarenes are bad ATRP initiators, ATRP can be carried out, e.g., in chlorobenzene. The fragment that forms the R-end of the polymer chain can contain a number of functional groups tolerant to ATRP catalysts and radicals.

The main role of the initiator is to determine the number of growing polymer chains. If initiation is fast and transfer and termination negligible, then the number of growing chains is constant and equal to the initial initiator concentration. The theoretical molecular weight or degree of polymerization (DP) increases reciprocally with the initial concentration of initiator in a living polymerization (2.8).

$$DP = [M]_0 / [\text{initiator}]_0 \times \text{conversion} \qquad (2.8)$$

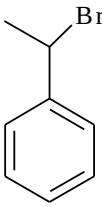
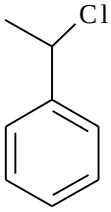
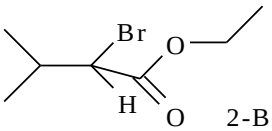
In ATRP, alkyl halides (RX) are typically used as the initiator and the rate of the polymerization is first order with respect to the concentration of RX. To obtain well-defined polymers with narrow molecular weight distributions, the halide group, X, must rapidly and selectively migrate between the growing chain and the transition-metal complex. Thus far, when X is either bromine or chlorine, the molecular weight control is the best. Initiation should be fast and quantitative with a good initiator. In general, any alkyl halide with activating substituents on the R-carbon, such as aryl, carbonyl, or allyl groups, can potentially be used as ATRP initiators.

Polyhalogenated compounds (e.g., CCl_4 and $CHCI_3$) and compounds with a weak R-X bond, such as N-X, S-X, and O-X, can also be used as ATRP initiators. The most frequently used initiator types used in the atom transfer radical polymerization systems are given in Table 2.1. When the initiating moiety is attached to macromolecular species, macroinitiators are formed and can be used to synthesize block/graft copolymers.

Similarly, the efficiency of block/graft copolymerization may be low if the apparent rate constant of cross-propagation is smaller than that of the subsequent homopolymerization. It should be noted, however, that R-X bonds can be cleaved not only homolytically but also heterolytically, which depends mostly on the initiator structure and the choice of the transition metal catalyst. For example, side reactions are observed for coppermediated ATRP of *p*-methoxystyrene, likely due to the

heterolytic cleavage of C-X bond or oxidation of the radical to the corresponding carbocation.

Table 2.1 Types of initiators used in ATRP sytems

Initiator	Monomer
 1-Bromo-1-phenyl ethane	Styrene
 1-Chloro-1-phenyl ethane	Styrene
 2-Bromo ethyl isobutyrate	Methylmethacrylate

2.1.2.2. Catalysts in ATRP

Perhaps the most important component of ATRP is the catalyst. It is the key to ATRP since it determines the position of the atom transfer equilibrium and the dynamics of exchange between the dormant and active species. There are several prerequisites for an efficient transition metal catalyst. Molecular weights and polydispersities with conversion for a living polymerization.

Various metals have been used: Cu, Fe, Ni, Ru, etc. Copper is the most frequently used metal in ATRP.

Importance of the ligand:

1. Solubilization of the metal ions

2. Influencing the redox potential of the metal (for ATRA it was shown that a low oxidation potential is required)

With copper various classes of ligands have been used:

1) (substituted) bipyridines

2) Schiff's bases of general structure

3) multidentate alifatic tertiary amines like

2.1.2.3. Monomers

ATRP has been mainly applied to styrene, (meth) acrylates and acrylates. However, it has also been used with other monomers like acrylonitrile and 4-vinyl pyridine. For each monomer, the reaction conditions are different since atom transfer equilibrium depends upon the combination of halide initiator and metal catalyst. Thus, metal complex and halide initiator are useful tools to fine tune ATRP. Acrylonitrile ATRP was reported with copper catalyst system. Ethylene carbonate was used as solvent and 2-bromopropionitrile was used as initiator to get polyacrylonitrile with $M_w/M_n <$ 1.01. Benzylic halides, when used as initiators, gave polymers with broad polydispersities. Poly (dimethylamino) ethyl methacrylate, a water-soluble and hence attractive polymer was synthesized using copper bromide complexed with different amine ligands as catalyst and ethyl 2-bromoisobutyrate or 2-bromopropionitrile as initiator in variety of solvents. This resulted in well-controlled polymerizations with low polydispersities at room temperature. Polymers with higher polydispersities were obtained in solvents in which catalyst was less soluble. Polymerizing 4-vinyl pyridine (4VP) by ATRP has been a major challenge since; 4VP is a strong binding ligand. Its competition with other ligands to bind with copper slows down rate of polymerization. Therefore, a much stronger binding ligand like PMDETA or tris [2-(dimethylamino) ethyl] amine (Me_6TREN) was used when Xia et al. [61] polymerized 4VP by ATRP mediated by copper catalyst.

For polymerization, protic solvents were required since they not only solubilize the catalyst but also decrease the contamination of catalyst by hydrogen bonding to 4VP/P4VP. A series of substituted styrene was polymerized in order to correlate monomer structure with rate of polymerization. Monomers with electron withdrawing substituents gave better polymerization control and faster rates than those with electron donating substituents since electron withdrawing substituents increase monomer reactivity and decrease stability of dormant species. Well-defined water-soluble polymers were synthesized by polymerizing monomethoxy capped oligo (ethylene oxide) methacrylate in aqueous media at 208°C using various

initiators. Other monomers polymerized by ATRP include 2-hydroxy ethyl acrylate, glycidyl acrylate, 2 hydroxy ethyl methacrylate, (meth) acrylamides, and vinyl acetate (using iron complexes) [56].

2.1.2.4. Solvents

ATRP can be carried out either in bulk, in solution, or in a heterogeneous system (e.g., emulsion, suspension). Various solvents, such as benzene, toluene, anisole, diphenyl ether, ethyl acetate, acetone, dimethyl nformamide (DMF), ethylene carbonate, alcohol, water, carbon dioxide, and many others, have been used for different monomers. A solvent is sometimes necessary, especially when the obtained polymer is insoluble in its monomer (e.g., polyacrylonitrile). Several factors affect the solvent choice. Chain transfer to solvent should be minimal. In addition, interactions between solvent and the catalytic system should be considered. Catalyst poisoning by the solvent (e.g., carboxylic acids or phosphine in copperbased ATRP) and solvent-assisted side reactions, such as elimination of HX from polystyryl halides, which is more pronounced in a polar solvent, should be minimized. The possibility that the structure of the catalyst may change in different solvents should also be taken into consideration. For example, the ATRP of n-butyl acrylate with $CuBr(bpy)_3$ (bpy = 2,2'-bipyridine; here and below the notation of the complex reflects only the stoichiometry of added reagents and not the structure of the complex) as the catalyst carried out in ethylene carbonate was found to proceed much faster than in bulk. A structural change from a dimeric halogen-bridged Cu(I) species in the bulk system to a monomeric Cu(I) species in ethylene carbonate was proposed to explain the rate difference. A similar rate enhancement in polar media was observed later from different studies. Polar media can also help to dissolve the catalyst. For example, homogeneous ATRP using $CuBr(bpy)_3$ was achieved using 10% v/v DMF [58].

2.1.2.5. Reaction conditions for ATRP

In ATRP, selection of appropriate reaction conditions depends upon targeted molecular weight, degree of polymer chain end-functionality, reactivity and structure of monomer and initiator, amount of catalyst or deactivator, and halogen end group as well as temperature. ATRP requires less stringent reaction conditions as compared to other living polymerization methods and being radical in nature, is a robust

technique i.e. it tolerates aqueous conditions, impurities, various functional groups in monomers, etc. and can be carried out in bulk or in solution. Usually, for most of the catalyst systems, temperature required is below 100°C except for copper-based systems. Recently, various attempts have been made to apply ATRP to other reaction conditions to make it a widely applicable process [56].

2.1.3. Iniferter method

Iniferters are initiators that induce radical polymerization that proceeds via initiation propagation, primary radical termination, and transfer to initiator. Because bimolecular termination and other transfer reactions are negligible, these polymerizations are performed by the insertion of the monomer molecules into the iniferter bond, leading to polymers with two iniferter fragments at the chain ends. The use of well-designed iniferters would give polymers or oligomers bearing controlled end groups. If the end groups of the polymers obtained by a suitable iniferter serve further as a polymeric iniferter, these polymerizations proceed by a living radical polymerization mechanism in a homogenous system. In these cases, the iniferters (C-S bond) are considered a dormant species of the initiating and propagating radicals. Iniferters can be classified into several types: thermal or photoiniferters; monomeric, polymeric or gel iniferters; monofunctional, difunctional, trifunctional or polyfunctional iniferters; monomer or macro monomeriniferters [50].

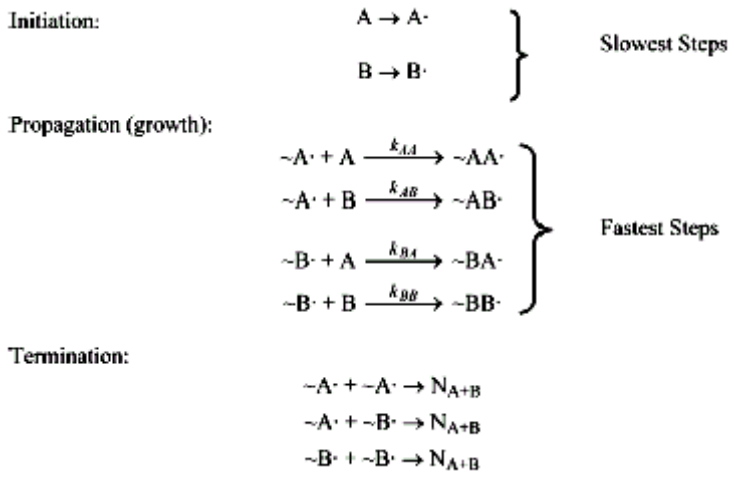
2.1.4. Copolymers

Copolymerization is a very useful process for synthesizing polymer with the required combination of properties and may be compared to alloying in metallurgy. Free-radical chain polymerization is the most common reaction mechanism, but other polymerization mechanisms also are possible, such as anionic and cationic polymerization. Free-radical chain polymerization can be obtained from mixtures of two or more monomers to form polymeric products that obtain two or more structures in the polymer chain, which is termed a copolymerization reaction to form a copolymer product. Polystyrene is a good example to exhibit the features and importance of the copolymerization process. Polystyrene is a brittle plastic with a low impact strength and low solvent resistance, but copolymerization greatly enhances these properties and the applications of polystyrene. Also, styrene

copolymers are useful not only as plastics but as elastomers. Thus, free-radical copolymerization of the styrene monomer with 20–35% by weight of the acrylonitrile monomer produces an enhanced impact and solvent resistant copolymer. The process of two monomers to form a copolymer in random arrangement.

The two monomer concentrations in the copolymer are determined by their relative initial concentrations and reactivities. The arrangement of monomer units in a copolymer can be random, alternative, block, or graft. For styrene–acrylonitrile copolymers, a random arrangement is the most common. The composition of the produced copolymer by simultaneous polymerization of two monomers is usually different from the composition of the monomer feed, which shows that different monomers have different tendencies to undergo copolymerization. These tendencies often have little or no resemblance to their behavior in homopolymerization.

A typical free-radical copolymerization reaction of two monomers, A and B, will follow the scheme of three steps: initiation, propagation, and termination, as presented in (2.9). It is well established today that initiation, growth, and termination are the principal, although not necessarily the only steps that determine the kinetics of free-radical chain polymerization/copolymerization reactions. The rates of these individual steps vary widely, but the propagation reactions are the most rapid. The initiation reaction, which produces an activated radical from a stable monomer, is by far the slowest step whenever long chains are formed.



(2.9)

From the four growth reactions in Fig. (2.9), the parameters r_A and r_B can each be defined as a monomer reactivity ratio and are represented as

$$r_A = k_{AA}/k_{AB} \quad \text{and} \quad r_B = k_{BB}/k_{BA} \tag{2.10}$$

The monomer reactivity ratio is the ratio of rate constants for a reactive propagating species addition to its own type of monomer to the rate constant for its addition to the other monomer. The monomer reactivity ratio can be considered to be the relative tendency for homopolymerization and cross-propagation copolymerization. Copolymers are subdiveded into block, gradient, random, periodic, segmented and graft copolymers [12]. Block copolymers are polymers which consist of two or more monomers that are segregated into separate regions of the polymer chain of the polymer chain, but are covalently bound to each other. Gradient copolymers exhibit a compositional gradient along the chain: one end of a bipolymer is enriched in first monomer unit and the other end in second monomer unit. Random copolymers have no continuous change in instantaneous compositon. In periodic copolymers, monomeric units are arranged in periodic sequences. Multiblock copolymers with short block lengths are known as segmented copolymers. In graft copolymers, the blocks are connected to the main chain as side-chains. Schematic representation of the compositon in block, gradient, random, periodic, segmented and graft copolymers, in which the open circles denote monomer 1 and the closed circles denote monomer is given in (2.11) [62].

Block

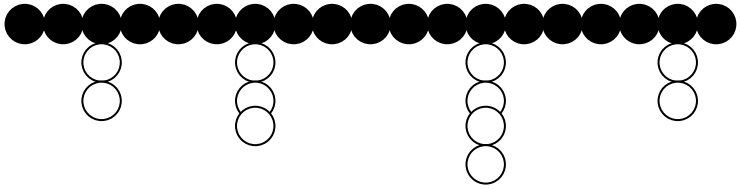
Gradient

Random

Periodic (2.11)

Segmented

Graft

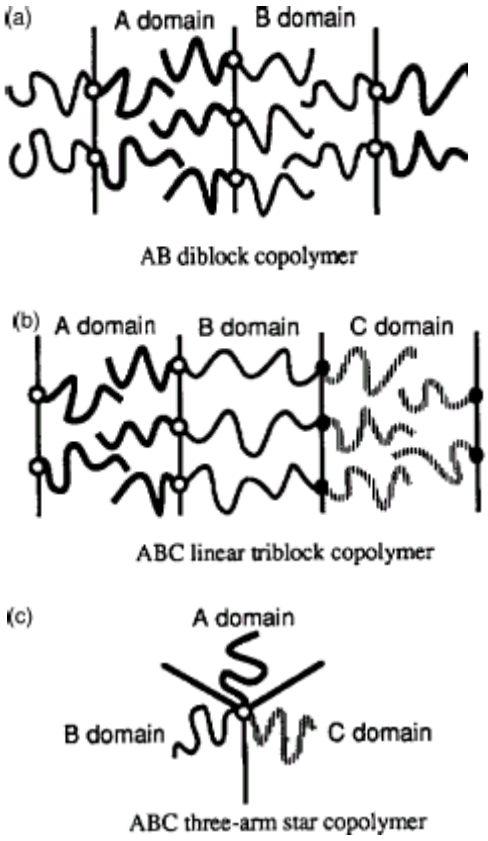


2.1.4.1. Block copolymers

Block copolymers have been the focus of intense scientific and commercial development because of their ability to organize into precise structures with a wide variety of morphology. Chemically joined two of more homopolymers result in the formation of block copolymers which, due to their incompatibility caused by different Flory–Huggins interaction parameter; undergo microphase separation from the disordered phase to a variety of ordered structures on the molecular scale of 5–100 nm. The segregation of these blocks into an interfacial region can create microdomains causing free energy minimisation. Experimental and theoretical measurements of block copolymers demonstrate the existence of three stable ordered morphologies in both the strong and weak segregation limits: alternating lamellae of A and B (LAM), hexagonally packed cylinders of A in a matrix of B (HEX) or the packing of spheres to give a body centre cubic (bcc) structure. The actual microdomain formed is determined by the competition between A and B blocks as to which of them would have to pay the entropic penalty to stretch. A flat interface is created due to competition between an identical volume fraction of each block. However, a curved interface is entropically favoured if two blocks are of dissimilar volume fractions and hence the larger block relaxes on the convex side and the smaller block on the concave side. Non-linear block copolymers, also known as star branched copolymers, consist of three or more identical or different arms extended outwardly from a nucleus generated by a multifunctional linking agent. Although rheological properties of star branched copolymers of narrow molar mass distribution are signifi- cantly different from those of linear polymer melts most of the rheological behaviour studied so far has encompassed linear block copolymers. Linear chains are constrained in a tube made up of the neighbouring molecules, which restricts the long-time motion of a chain to curvilinear diffusion along its own contour. This dynamic mode is termed reptation. However, stress in star polymers

relaxes by arm retraction and arms explore new configurations by retracting along their tubes and ‘poking’ out again in a new direction.

Block copolymers can be divided into three classes: (a) those with new linear chain architecture; (b) linear terpolymers with three chemically different blocks; and (c) mixtures of linear diblocks with molecular weight or compositional difference [56].



3. EXPERIMENTAL PART

3.1. Chemicals Used

Styrene (St) (99%, Aldrich) was passed through basic alumina columns to remove inhibitors and then dried over CaH_2 and distilled *in vacuo* prior to use. *n*-Butyl acrylate (*n*-BA) and acrylonitrile (AN) were obtained from Aldrich; the inhibitor was removed by passing through a column of basic alumina.

Tetrahydrofuran (THF) [99.8%, J.T. Baker high pressure liquid chromatography grade] was dried and distilled over $LiAlH_4$. All other reagents were purchased from Aldrich and used as received.

2-Phenyl-2-[(2,2,6,6-tetramethylpiperidino)oxy]-1-ethanol was synthesized according to the procedure of Hawker [65]. (92%). ^{1}H-NMR ($CDCl_3$) δ 1.15-1.58 (m, 18H), 3.72 (d of d, J=2.5 and 12 Hz, 1H, CH_2), 4.22 (d of d, J=9.5 and 12 Hz, 1H, CH_2), 5.31 (d of d, J=2.5 and 9.5 Hz, 1H, CH), 5.89 (br s, OH), 7.29-7.36 (m, 5H, ArH). ^{13}C-NMR ($CDCl_3$) δ 17.25, 20.66, 25.64, 32.20, 34.21, 39.99, 40.52, 61.03, 67.93, 84.23, 126.96, 127.83, 128.31, 139.1

3.2. Synthesis of 2-phenyl-2-[(2,2,6,6-tetramethylpiperidino)oxy] ethyl 2-bromo propanoate,(1)

To a round bottom flask were added 2-Phenyl-2-[(2,2,6,6-tetramethylpiperidino)oxy]-1-ethanol (2,24 g, 3,06 mmol), triethylamine (Et_3N) (1,84 ml, 13,14 mmol), and 30 ml of dry tetrahydrafuran (THF). To the reaction mixture, stirred at room temperature under nitrogen was added drop wise 2-bromopropanoyl bromide (1,4 ml, 13,21 mmol) in 20 ml of dry THF over a period of one hour. The reaction mixture was stirred at room temperature overnight. The salt was removed by filtration and after THF evaporation, the crude product was dissolved in dichloromethane (CH_2Cl_2) and washed successively with excess K_2CO_3 aqueous solution and water. Then dried over anhydrous Na_2SO_4, CH_2Cl_2 was

removed and the crude ester was passed through a column of silica gel using hexane as the eluent. The resulting material was obtained as a pale yellow oil (1,8 g, 54%).

3.3. Synthesis of Polystyrene and Polyacrylonitrile Macroinitiators

Polyacrylonitrile (PAN) macroinitiator was prepared by ATRP of acrylonitrile using CuBr/bpy as catalyst, ethylene carbonate (EC) and 1 as initiator at 60^{o}C. To a Schlenk tube equipped with magnetic stirring bar, the degassed monomer, ligand, catalyst, ethylene carbonate and initiator were added in the order mentioned. Tube was degassed by three freeze-pump-thaw cycles, left under vacuum and placed in a thermostated oil bath at given temperature. After the polymerization, the reaction mixture was diluted with DMF and then passed through a column of neutral alumina to remove metal salt and the polymer was precipitated into a large excess of methanol solution, and dried.

Polystyrene (PS) macroinitiator was prepared by NMP in the presence of 1. The reaction mixture was degassed by three freeze-pump-thaw cycles and polymerized at 125^{o}C for given time. The polymerization mixture was diluted with THF and precipitated in methanol.

3.4. Copolymerization of Styrene and Acrylonitrile (SAN) Using Difunctional Initiator (1) by ATRP

In a typical experiment first, the monomers (St and AN), 2,2'-bipyridine (bpy), CuBr, diphenylether (DPE) and 1 were added in a dry Schlenk tube equipped with a magnetic stirring bar. The tube was degassed by three freeze-pump-thaw (FPT) cycles left under vacuum and placed in an oil bath thermostated at 90°C. After the polymerization, the final reaction mixture was diluted with THF and then the solution was filtered through a column filled with neutral alumina, and the copolymers were precipitated in excess of hexane.

3.5. Synthesis of Diblock Copolymers

3.5.1. Synthesis of poly(St-*b*-AN) diblock copolymer

The procedure for the synthesis of diblock copolymers are as follows; the polymerization of AN was carried out in a Schlenk tube equipped with magnetic stirring bar. A given amount of AN, CuCl, Bpy, EC, DMF (AN/EC = 1; v/v) and PS as macroinitiator was added to the tube in the order mentioned. Tube was then subjected to freeze-pump-thaw cycles three times to remove dissolved gas. The polymerization was conducted at 70^{o}C for given times. After the polymerization, the reaction mixture was diluted with THF and then passed through a column of neutral alumina to remove metal salt. The excess of THF and unreacted monomer was evaporated under reduced pressure. The resulting polymer was dissolved in THF, precipitated in excess of methanol and then isolated by vacuum filtration.

3.5.2. Synthesis of poly (St-*b*-BA) diblock copolymer

Poly(St-*b*-BA) block copolymer was prepared by ATRP of nBA using CuBr/Bpy as catalyst and polystyrene as macroinitiator. The polymerization was carried out at 70^{o}C under degassed condition for given times. The purification was as described above for the diblock copolymers.

3.5.3. Synthesis of poly (AN-*b*-St) diblock copolymer

Poly (AN-*b*-St) diblock copolymer was prepared by NMP of St. Alkoxyamine-ended PAN macroinitiator was dissolved with DMF in a Schlenk tube. After, St was added to the tube. Then the tube was placed in an oil bath at 125 °C. After, the reaction mixture was diluted with THF and precipitated in methanol.

3.5.4. Chain Extension of SAN to prepare block copolymer containing random SAN sequences and St by NMP

TEMPO terminated SAN copolymer was dissolved with St in a Schlenk tube. After, the tube was subjected to three FPT cycles. Then, the flask was placed in an oil bath set at 125°C. After the polymerization, the reaction mixture was dissolved in THF, and the polymer was precipitated by adding into methanol solution. The solid products were dried in a vacuum, yielding the desired block copolymer (SAN-*b*-PS).

3.5.5. Copolymerization of Styrene and Acrylonitrile using PS macroinitiator by ATRP:

First, the monomers (St and AN) were placed in a Schlenk tube. Then, Bpy, CuBr, $CuBr_2$, DPE and bromine-terminated PS were added into the Schlenk tube. The tube was degassed by FPT cycles. The tube was finally placed in an oil bath at 80°. At the end, the final reaction mixture was diluted with THF, the solution was filtered through a column filled with neutral alumina, and the block copolymer was precipitated in excess methanol. The solid products were dried in a vacuum, yielding the desired block copolymer (PS-*b*-SAN).

3.6. Synthesis of Triblock Copolymers

3.6.1. Synthesis of poly (St-*b*-BA-*b*-AN) triblock copolymer

The procedure for the synthesis of triblock copolymers are as follows; the polymerization of AN was carried out in a Schlenk tube equipped with magnetic stirring bar. A given amount of AN, CuCl, Bpy, EC, DMF (AN/EC = 1; v/v) and PS-*b*-PBA as macroinitiator was added to the tube in the order mentioned. Tube was then subjected to freeze-pump-thaw cycles three times to remove dissolved gas. The polymerization was conducted at 70^{o}C for given times. After the polymerization, the reaction mixture was diluted with THF and then passed through a column of neutral alumina to remove metal salt. The excess of THF and unreacted monomer was evaporated under reduced pressure. The resulting polymer was dissolved in THF, precipitated in excess of methanol and then isolated by vacuum filtration.

3.7. Instrumentation

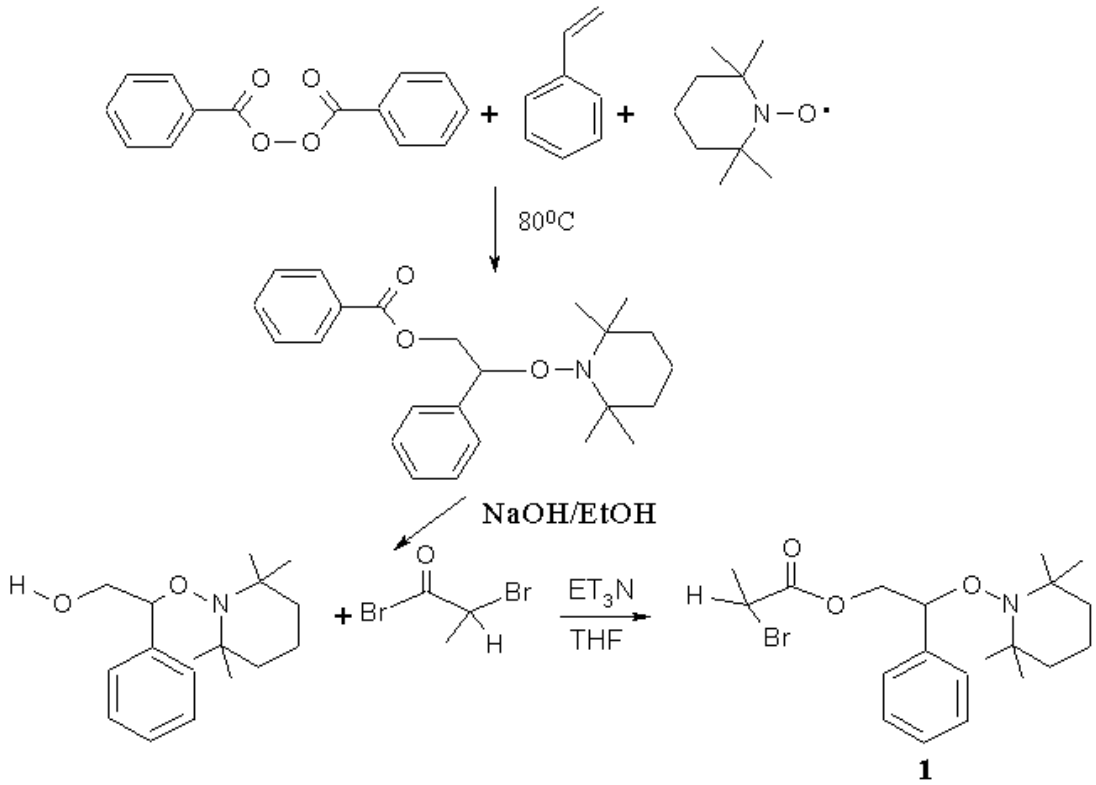
The number-average molecular weights (M_n) and polydispersity index (M_w/M_n) were measured with gel permeation chromatography (GPC) on a Agilent Model 1100 instrument containing a pump, a refractive index detector and four Waters Styragel columns HR 5E, HR 4E, HR 3, HR 2; and THF was used as eluent at a flow rate of 0.3 mL/min at 30 ^{o}C. Data analysis was performed with PL Caliber software. The system was calibrated with narrow polystyrene standards (Polymer Laboratories). The ^{1}H NMR spectra were recorded on a Bruker NMR spectrometer (250 MHz). The

FT-IR analysis was performed using Perkin Elmer Spectrum One B FT-IR Spectrometer.

4. RESULTS AND DISCUSSIONS

4.1. Synthesis of Initiator

4.1.1. Synthesis of 2-phenyl-2-[(2,2,6,6- tetramethylpiperidino)oxy]ethyl 2-bromo propanoat, (1)



Scheme 4.1: Synthesis of 2-phenyl-2-[(2,2,6,6-tetramethylpiperidino)oxy]ethyl 2-bromo propanoat, (1)

1-(benzyloxy)-2-phenyl-2-(2',2',6',6'-tetramethyl-1-piperidinooxy)ethane was synthesized according to the procedure reported by Hawker et al. [62].

First of all, the synthesis of benzoic acid 2-phenyl-2-(2,2,6,6-tetramethyl-piperidin-1-yloxy)-ethyl ester (1) was carried out by heating styrene in the presence of benzoyl peroxide and TEMPO for 30 minutes. The hydrolysis of ester was then carried out to give the 2-phenyl-2-(2, 2, 6, 6-tetramethyl-piperidin-1-yloxy)-ethanol (2). The characteristic peak of aromatic protons adjacent to ester group at δ 7.9 ppm completely disappeared after hydrolysis. Moreover, the new signals appeared at δ 5.9

ppm of –OH and the shifts of the $–CH_2$ and –CH protons adjacent to hydroxyl and aromatic group, respectively, clearly confirm the successful hydrolysis.

The asymmetric difunctional initiator, (1), was prepared from tempo alcohol and corresponding acid bromide in ca 54% yield. The obtained initiator, (1), was then characterized by ^{1}H-NMR. The ^{1}H-NMR spectra of the initiator showed no signal corresponding to OH protons of the starting tempo alcohol, indicating quantitave esterification (Figure 4.1).

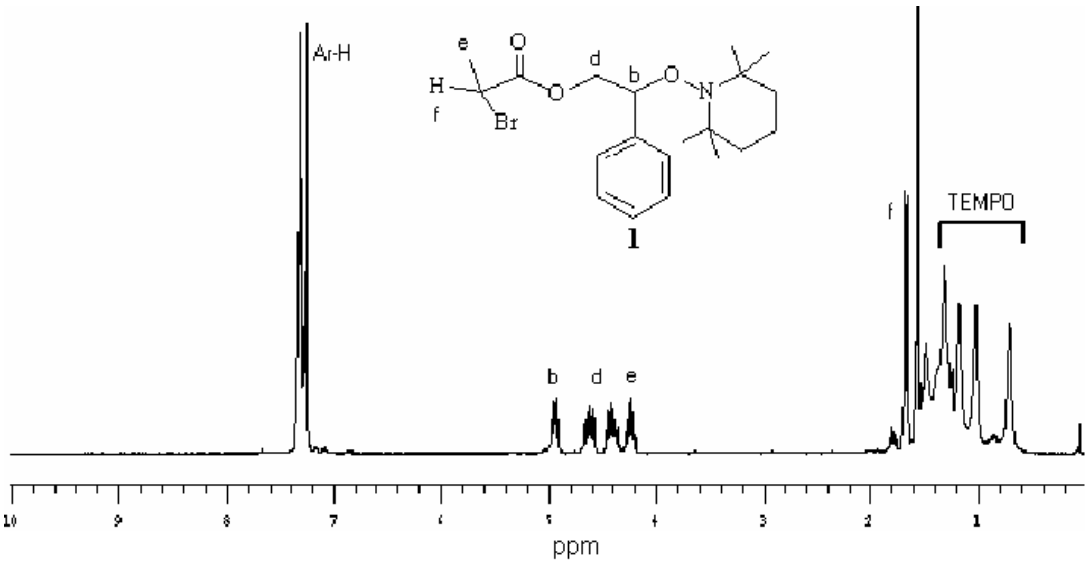


Figure 4.1: The 1H-NMR spectra of the initiator, (1), 2-phenyl-2-[(2,2,6,6-tetramethylpiperidino)oxy]ethyl 2-bromo propanoat

4.2 Synthesis of Poly (acrylonitrile, PAN) and Poly (styrene, PS) Macroinitiators

2-phenyl-2-[(2,2,6,6-tetramethylpiperidino)oxy]ethyl 2-bromo propanoat, (1) was used to perform the controlled radical polymerization of AN and nitroxide mediated radical polymerization of St. Poly(acrylonitrile) homopolymers with different molecular weights were synthesized via controlled radical polymerization polymerization of AN in solution at 60°C. The polymerization was initiated by 1 catalyzed by the CuBr/Bpy. This led to formation of bromine terminated PAN macroinitiator with narrow polydispersity. The results are tabulated in Table 4.1.

Theoretical molecular weights calculated from;

$$M_{n,\,theo} = [M]_0/[I]_0 \text{ x conv\% x } M_w\,(AN) + M_{n,initiator} \quad (1)$$

Table 4.1. Sythesis of PAN macroinitiator by ATRP route.

RUN	Initiator	$[M]_o/[I]_o$	Time (h)	Temp (^oC)	Conv (%)	$M_{n,GPC}$[b]	$M_{n,\ theo}$	M_n ^{1}H NMR	M_w/M_n
PI[a]	1	70	3.6	60	67	-	3000	4400	1.65
PII[a]	1	40	2.3	60	95	-	2440	2570	1.05

a) $[I]_o/[CuBr]_o/[bpy]_o=1/1/3$

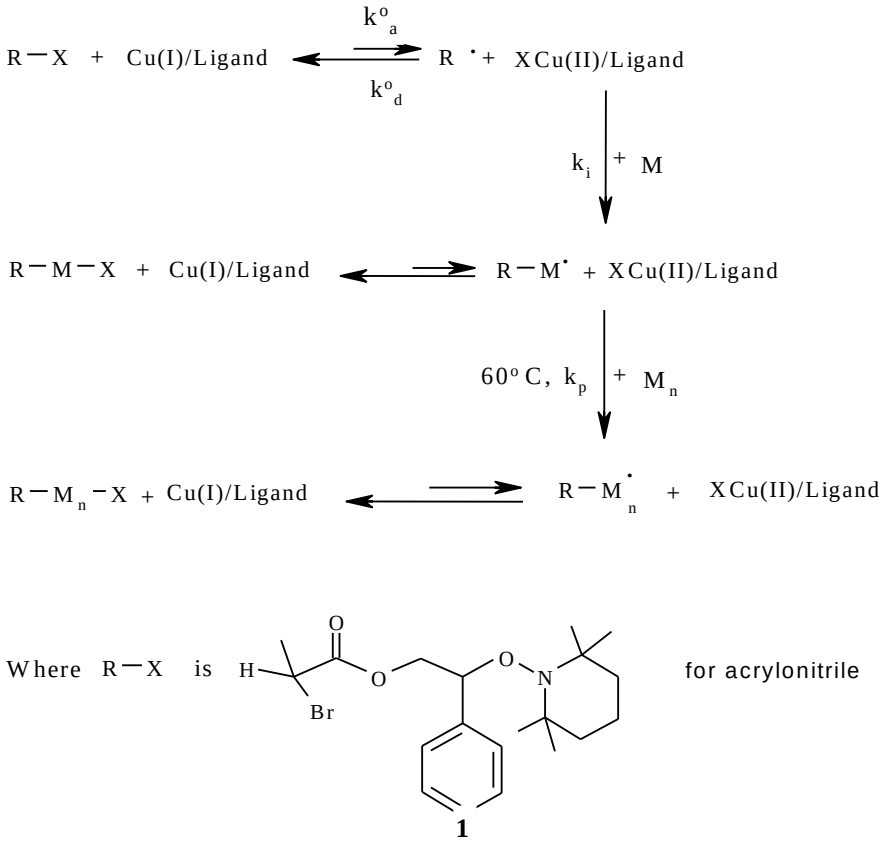
b) The molecular weights were calculated by the aid of linear PS standards

The conversions were calculated gravimetrically by the following formula;

% Conv = (W / M) x 100

Where W represents the weight of the formed polymer and M stands for the mass of the monomer initially taken.

These results imply that polymerization of AN proceeds in controlled manner with high initiation efficiency using 1 as initiator and CuBr/Bpy as heterogeneous catalyst system.



Ligand=Bpy; M represents the monomer

Scheme 4.2. Atom transfer radical polymerization (ATRP) of PAN as a schematic representation.

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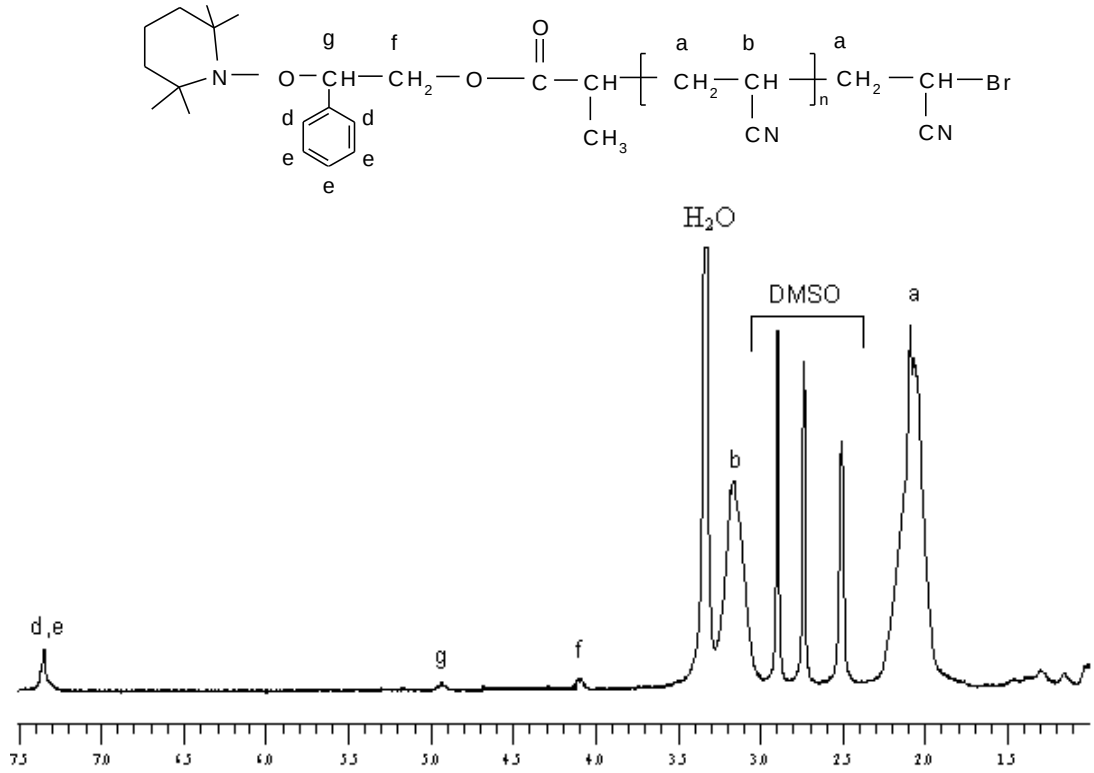
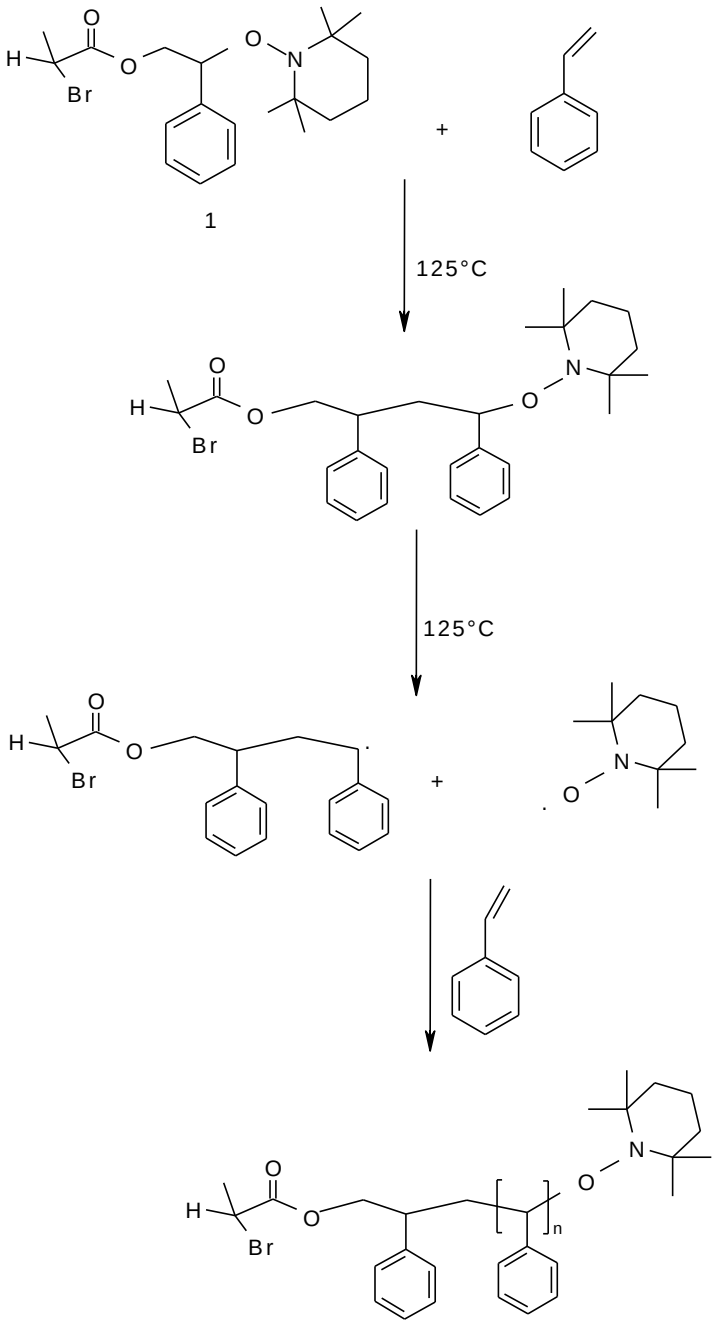


Figure 4.2. ^{1}H-NMR spectrum of PAN homopolymer in $CDCl_3$ at 25 °C

The spectrum of PAN shows two signals for the resonance of methylene proton at 2.0 ppm and methine proton at 3.1 ppm and shows the appearance of multiplet resonance at 7.4 ppm corresponding to the aromatic protons of styrene.



Scheme 4.3. Nitroxide mediated radical polymerization (NMP) of styrene as a schematic representation

Synthesis of polystyrene (PS) macroinitiator was prepared by NMP of styrene (St) in bulk at 125^0C in the presence of difunctional initiator (1).

4.3. Copolymerization of Styrene and Acrylonitrile (SAN) Using Difunctional Initiator (1) by ATRP

Difunctional initiator (1) has been used for the copolymerization of St and AN by ATRP using CuBr/bpy catalyst system at 90 ^{o}C. In all copolymerization experiments an azeotropic feed composition of St and AN was used (ca. 63 mol % St) [10]. The other conditions and results are given in Table 4.2. The synthetic strategy followed for the preparation of SAN copolymers and related block copolymers via the sequential ATRP-NMP route and vice versa with 1 as the initiator is depicted in Scheme 4.4.

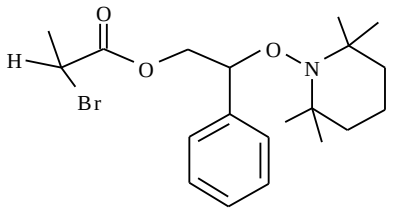
Although the initiator (1) used in the preparation of SAN copolymers does not have structures resembling closely those of the polymer chain end with AN or St terminal monomer unit, the control over the copolymerization of St/AN has been proved.

Table 4.2. Characteristics of copolymerization of St and AN via ATRP.

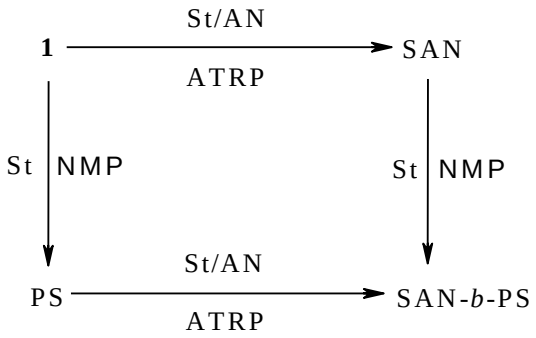
RUN	Initiator	Time (h)	Conversion (%)	$M_{n,GPC}$[b]	M_w/M_n	%PAN	
						^{1}H NMR	FTIR
I[a]	1	2	24	2530	1.34	-	-
II[a]	1	3	40	3530	1.29	-	-
III[a]	1	4.5	59	5460	1.23	20	37
IV[a]	1	6.5	85	7070	1.18	17	18

a) $[St]_o/[AN]_o/[I]_o/[CuBr]_o/[bpy]_o$= 25.3/14.9/1/0.5/1. The polymerization was carried out at 90 °C in DPE.

b) The molecular weights were calculated by the aid of linear PS standards.



1



Scheme 4.4. The schematic presentation of polymerization route to SAN copolymer and SAN-*b*-PS.

The molecular weight evolution, M_n as well as polydispersity index (PDI, M_w/M_n), as a function of monomer conversion are shown in Figure 4.2(b). In this case, M_n increased linearly with monomer conversion and low polydispersities ($M_w/M_n < 1.3$) were obtained (Fig.4.2 (b)), which indicates the constant concentration of growing chains present throughout the polymerization reaction. The variation of ln $[M]_o/[M]$ (where $[M]_o$ is the initial concentration of both the monomers and [M] is the concentration of both the monomers at the measured time) with time (Fig. 4.2(a)) shows linearity, which could be attributed to a constant number of active propagating chains throughout the reaction. As can be seen in Figure 4.3, the GPC traces of the copolymers remained monomodal and symmetrical. The ^{1}H-NMR spectrum of SAN copolymer shows the appearance of multiplet resonance at 6.5-7.4 ppm corresponding to the aromatic protons of styrene. The signal at 2.16 ppm is assigned to AAA. The signal at 1.84 ppm and 1.56 ppm are assigned to AAS and SSA, respectively (A and S are referred to acrylonitrile and styrene structural units, respectively).

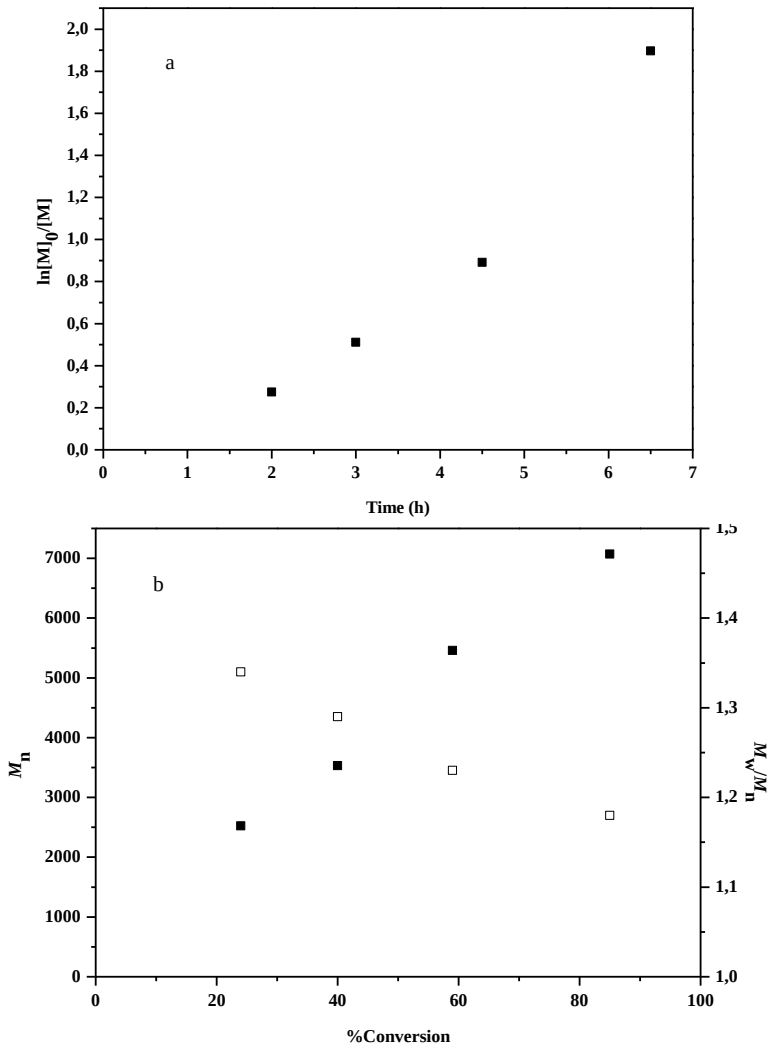


Figure 4.3. Semilogarithimic kinetic plot (a) for the ATRP of St/AN at 90°C. $[St]_o/[AN]_o/[I]_o/[CuBr]_o/[bpy]_o$=25.3/14.9/1/0.5/1 and (b) plot of M_n and M_w/M_n as a function of conversion.

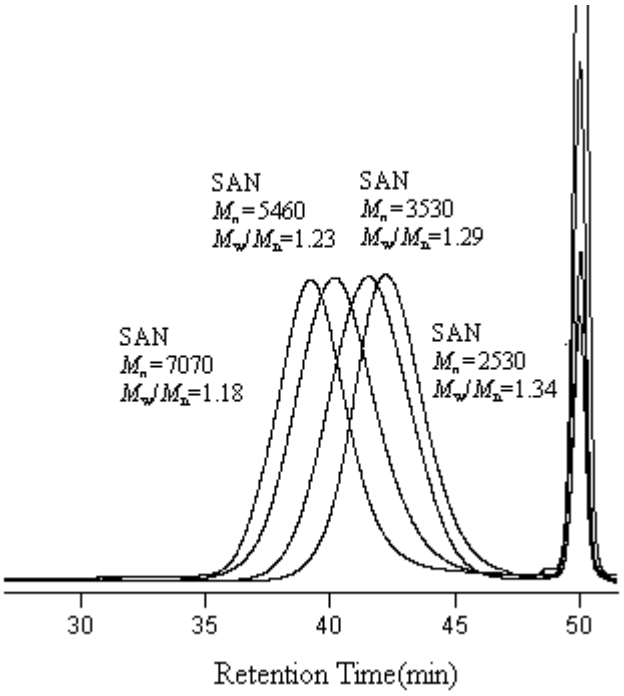


Figure 4.4. Evolution of GPC traces for SAN copolymers.

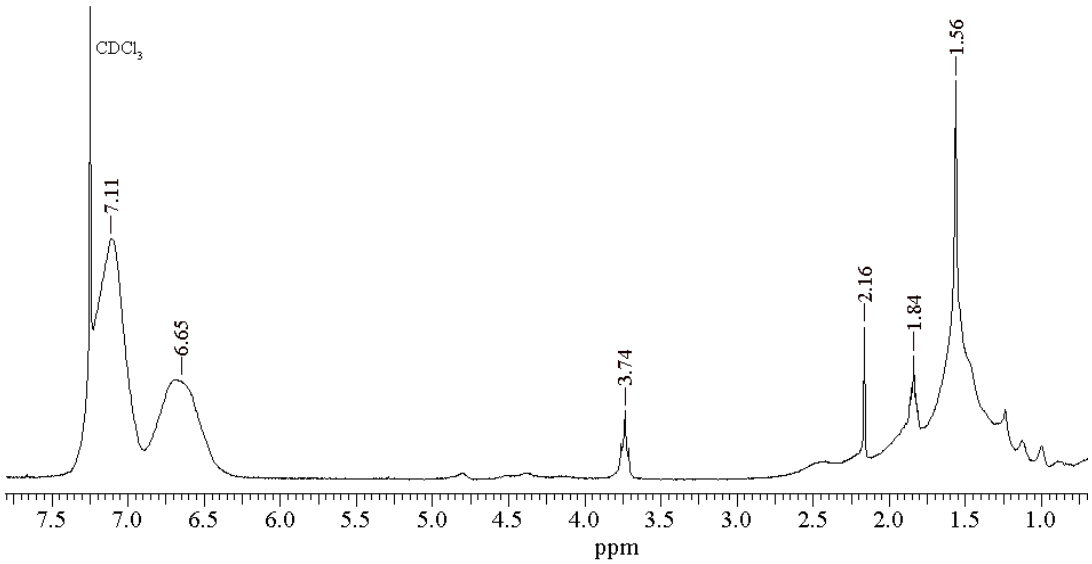


Figure 4.5. ^{1}H-NMR spectrum of SAN copolymer in $CDCl_3$ at 25 °C

4.4. Synthesis of Diblock Copolymers

4.4.1. Chain extension of SAN by NMP

Chain extension reactions of TEMPO-terminated SAN copolymers leading to block copolymers have been performed by NMP of St at 125 ^{o}C. In all chain extension reactions, well-defined block copolymers were obtained. The results for the synthesis of block copolymers by using SAN copolymer as a macroinitiator by NMP of St are listed in Table 4.3. There is a good agreement between the theoretical molecular weights calculated from $M_{n,\,theo} = [M]_o/[I]_o$ x conv. % x M_w (St) + $M_{nmacroinitiator}$ and the calculated ones from GPC. As can be seen in the Figure 4.6, a clear shift in molecular weight was observed. In addition, there was no indication of bimodality and the absence of the SAN macroinitiator peak on the GPC trace of block copolymer indicated that the macroinitiator was fully converted to the block copolymer. This result reveals that NMP of St using TEMPO-terminated SAN copolymer proceeds in a controlled manner with high initiation efficiency. Figure 4.7 shows the ^{1}H-NMR spectrum of SAN-*b*-PS.

Table 4.3. Characteristics of chain extension of SAN copolymer by NMP.

RUN	Initiator	$[M]_o/[I]_o$	Time (h)	Temp (^{o}C)	Conv (%)	$M_{n,GPC}$[b]	$M_{n,theo}$	M_w/M_n	% PAN ^{1}H NMR
IV[a]	1	-	6.5	90	95	7070	-	1.18	17
V	IV	200	20	125	39	15500	15150	1.16	24
VI	IV	50	6	125	15	7900	7850	1.12	-

a) $[St]_o/[AN]_o/[I]_o/[CuBr]_o/[bpy]_o$=25.3/14.9/1/0.5/1.

b) The molecular weights were calculated by the aid of linear PS standards.

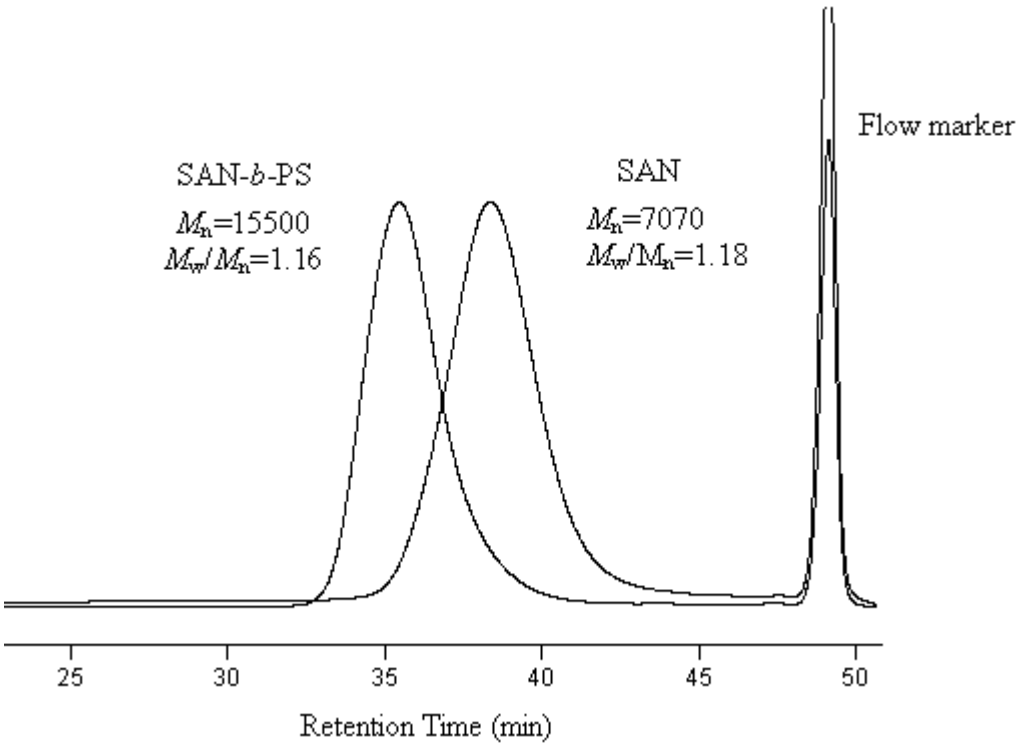


Figure 4.6. GPC traces for SAN copolymer and SAN-*b*-PS

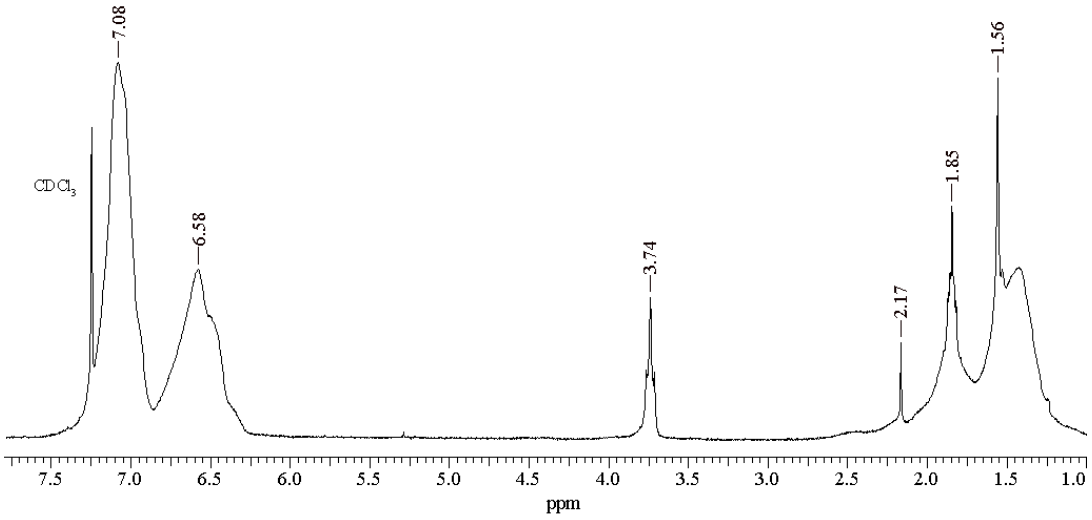


Figure 4.7. ^{1}H-NMR spectrum of SAN-*b*-PS block copolymer in $CDCl_3$ at 25 °C

4.4.2. Copolymerization of Styrene and Acrylonitrile using PS macroinitiator by ATRP

Different sequences of the polymerization processes can also be used to yield the structurally same block copolymers (Scheme 4.4). For this purpose, first NMP of St was carried out in bulk at 125 °C. In Table 4.4, there is good agreement between the theoretical molecular weight calculated from $M_{n,theo}$= $[M]_o/[I]_o$ x conv. % x M_w (St) + $M_{n,initiator}$ (1) and the molecular weight determined by GPC. These results indicate

that high initiation efficiency (f = 0.98) was obtained in our experimental condition using 1 as an initiator.

Table 4.4. Characteristics of copolymerization of St and AN using PS as macroinitiator by ATRP.

RUN	Initiator	$[M]_o/[I_o]$	Time (h)	Temp (°C)	Conv (%)	$M_{n,GPC}$ [b]	M_{ntheo}	M_w/M_n	% PAN FTIR
VII	1	100	17	125	49	5670	5550	1.23	-
VIII[a]	VII	-	6	80	-	7360	-	1.16	13

a) $[St]_o/[AN]_o/[I]_o/[CuBr]_o/[bpy]_o/[CuBr_2]_o$=50/25/1/1/1/0.08.

b) The molecular weights were calculated by the aid of linear PS standards.

ATRP of St/AN was performed using $CuBr/CuBr_2$/bpy as a catalyst and bromine-terminated PS macroinitiator at 80 °C in ethylene carbonate. The GPC traces of PS macroinitiator and PS-*b*-SAN are portrayed in Figure 4.8. There is a clear shift in GPC traces indicating that the incorporation of second block. The composition of block copolymer was determined via FTIR measurements.

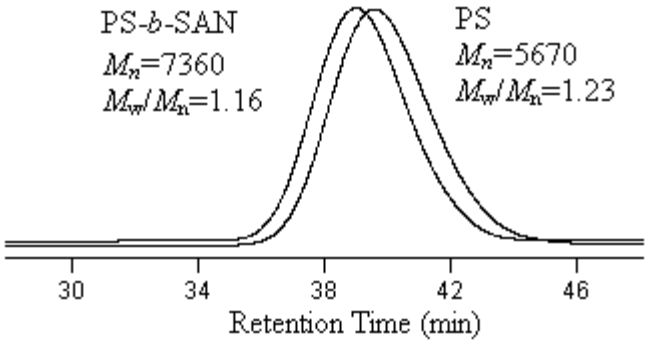


Figure 4.8. GPC traces for PS macroinitiator and PS-*b*-SAN

4.4.3. Synthesis of PS-*b*-PAN diblock copolymers by NMP-ATRP route

The previously obtained bromine-terminated PS was used as macroinitiator for ATRP of AN with CuCl/bpy catalyst system at 70 °C in DMF to afford PS-*b*-PAN diblock copolymers. The other results and conditions are tabulated in Table 4.5.

Table 4.5. Synthesis of PS-*b*-PAN by NMP-ATRP route.

RUN	Initiator	$[M]_o/[I]_o$	Time (h)	Temp (°C)	Conv (%)	M_{ntheo}[b]	M_w/M_n	% PAN ^{1}H NMR
XVIII	1	100	20	125	36	3750	1.20	-
VII	1	100	17	125	49	5550	1.23	-
IXX[a]	XVIII	400	5.25	70	13	7140	1.10	-
XV[a]	VII	400	8	70	25	10970	1.12	19
XVI[a]	VII	400	17	70	35	13060	1.17	37

a) $[I]_o/[CuCl]_o/[bpy]_o=1/1/2$

b) The molecular weights were calculated by the aid of linear PS standards.

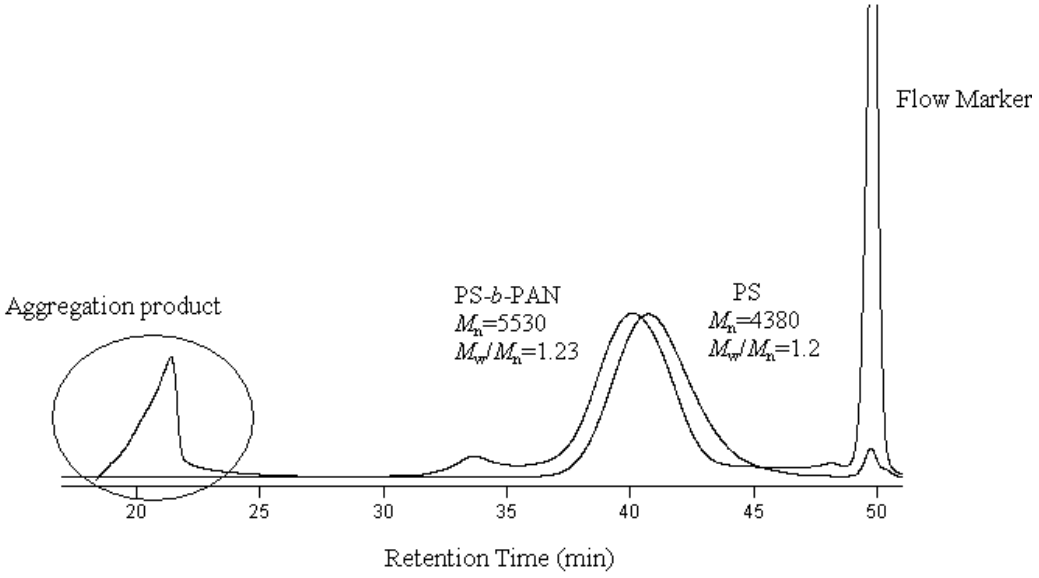


Figure 4.9. GPC traces for PS macroinitiator and PS-*b*-PAN

The GPC traces of PS macroinitiator and PS-*b*-PAN are portrayed in Figure 4.9. There is a clear shift in GPC traces indicating that the incorporation of second block and an aggregation product formed. PS-*b*-PAN is a worthwhile challenge because of the different polarities and solubilities of the blocks, and the expected mechanical properties, which could be compared with SAN copolymer and block copolymers. PS-*b*-PAN doesn't dissolve in THF exactly because THF is not good solution for PAN arm of block copolymer, but DMF is, so when THF was added to dissolve the polymer, PAN segments aggregated in THF solution. Finally, an aggregation product formed in GPC traces.

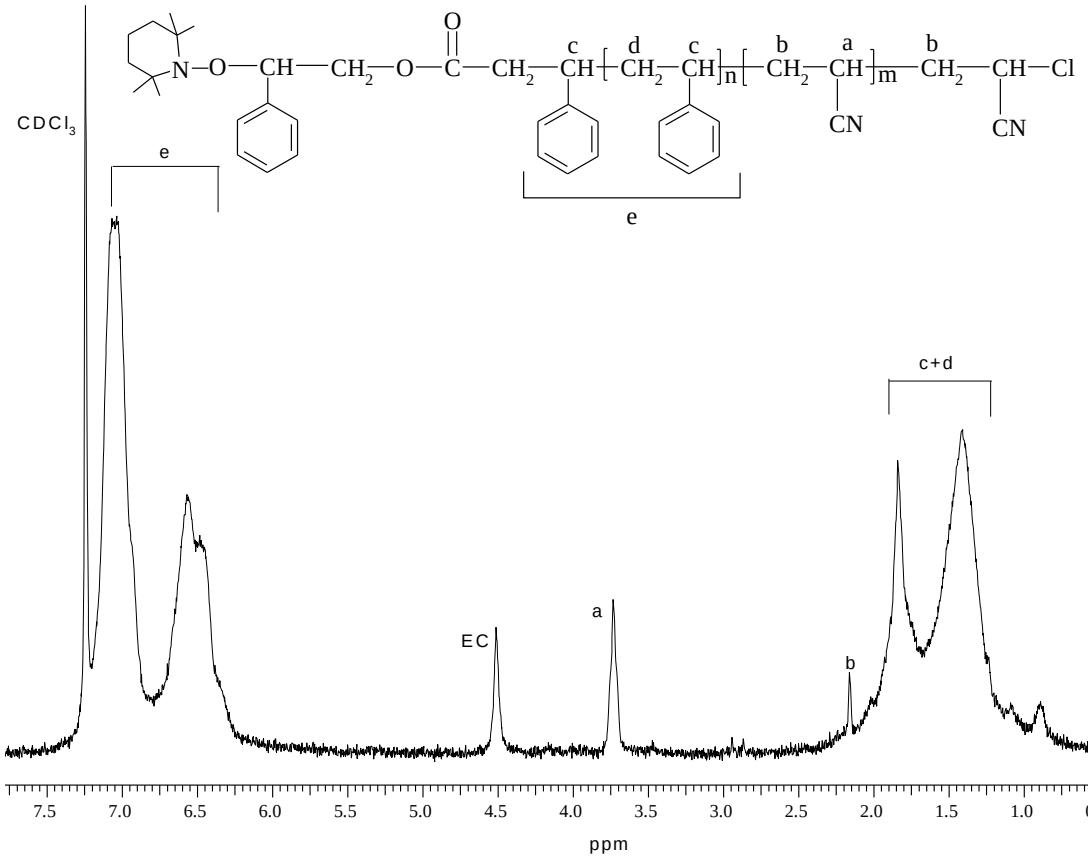


Figure 4.10. ^{1}H-NMR spectrum of PS-*b*-PAN block copolymer in $CDCl_3$ at 25 °C.

4.4.4. Synthesis of PAN-*b*-PS diblock copolymers by ATRP-NMP route

The previously obtained bromine-terminated PAN was used as macroinitiator for NMP of St 125 °C in bulk to afford PAN-*b*-PS diblock copolymers. The other results and conditions are tabulated in Table 4.6.

Table 4.6. Synthesis of PAN-*b*-PS by ATRP-NMP route.

RUN	Initiator	$[M]_o/[I]_o$	Time (h)	Temp (^{o}C)	Conv (%)	$M_{n,GPC}$ [b]	M_{ntheo}	M_n ^{1}H NMR	M_w/M_n
PI[a]	1	70	3.6	60	67	-	3000	4400	1.65
PIII	PI	440	40	125	35	18700	20440	-	1.31
PIV	PI	220	21.5	125	48	13800	15400	-	1.56

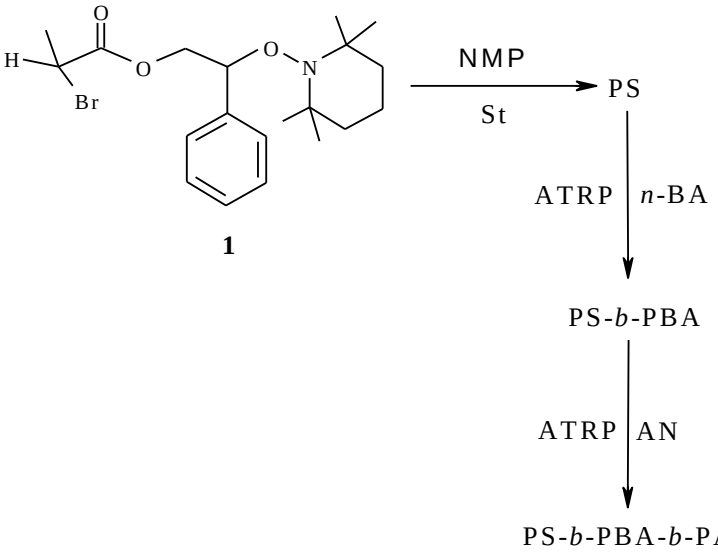
a) $[I]_o/[CuBr]_o/[bpy]_o$=1/1/3

b) The molecular weights were calculated by the aid of linear PS standards.

4.5. Synthesis of Triblock Copolymers

4.5.1. Synthesis of PS-*b*-PBA-*b*-PAN triblock copolymers

The synthetic strategy followed for the preparation of PS-*b*-PBA-*b*-PAN triblock copolymers via the NMP-ATRP-ATRP route while using 1 is depicted in Scheme 4.5. The other conditions and results are given in Table 4.7. First, previously obtained bromine-terminated PS (Table 4.7, entry 4) was used as macroinitiator for ATRP of n-BA at 70 °C. This led to PS-*b*-PBA diblock copolymers with predetermined molecular weight and low polydispersity. The experimental molecular weights were determined by GPC on the basis of linear PS standards. Although the hydrodynamic volume of PBA is not as same as those of linear PS standards, the resulting experimental molecular weight agreed with the theoretical molecular weight calculated from $M_{n,\,theo} = [M]_o/[I]_o$ x conv.% + M_w (nBA). Second, bromine-terminated diblock copolymers (PS-*b*-PBA) were further extended via ATRP of AN with CuCl/bpy catalyst system at 70°C to afford PS-*b*-PBA-*b*-PAN triblock copolymers.



Scheme 4.5. The schematic presentation of polymerization route to PS-*b*-PBA-*b*-PAN

The GPC trace of triblock copolymer is shown in Figure 4.11, together with the diblock copolymer and PS macroinitiator. The clear shift was observed from the GPC trace of triblock copolymer, XI (Fig. 4.11), when compared with that of diblock copolymer, X, implying that successive formation of triblock copolymer. ^{1}H NMR analysis allowed the determination of composition and molecular weights of block

copolymers. The ^{1}H NMR spectra of PS-*b*-PBA-*b*-PAN triblock copolymers exhibit major peaks that are characteristic of the St, nBA and AN segments (Figure 4.12). The molecular weights were calculated from the integration of signals between 6.5 and 7.0 ppm of PS (aromatic protons) and 4.02 ppm of PBA (OCH_2) to 3.74 ppm (CH) of PAN.

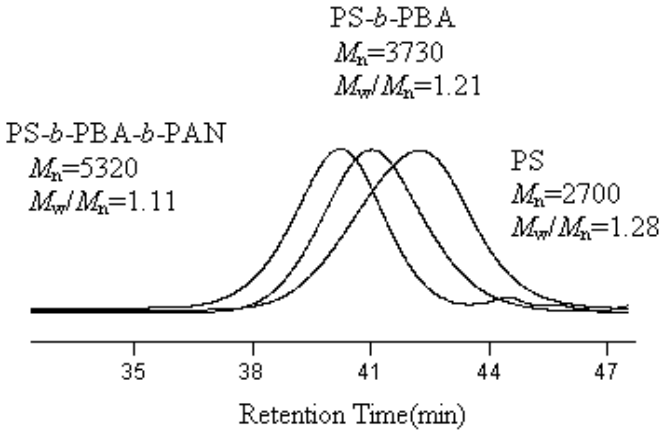


Figure 4.11. GPC traces for PS, PS-*b*-PBA and PS-*b*-PBA-*b*-PAN

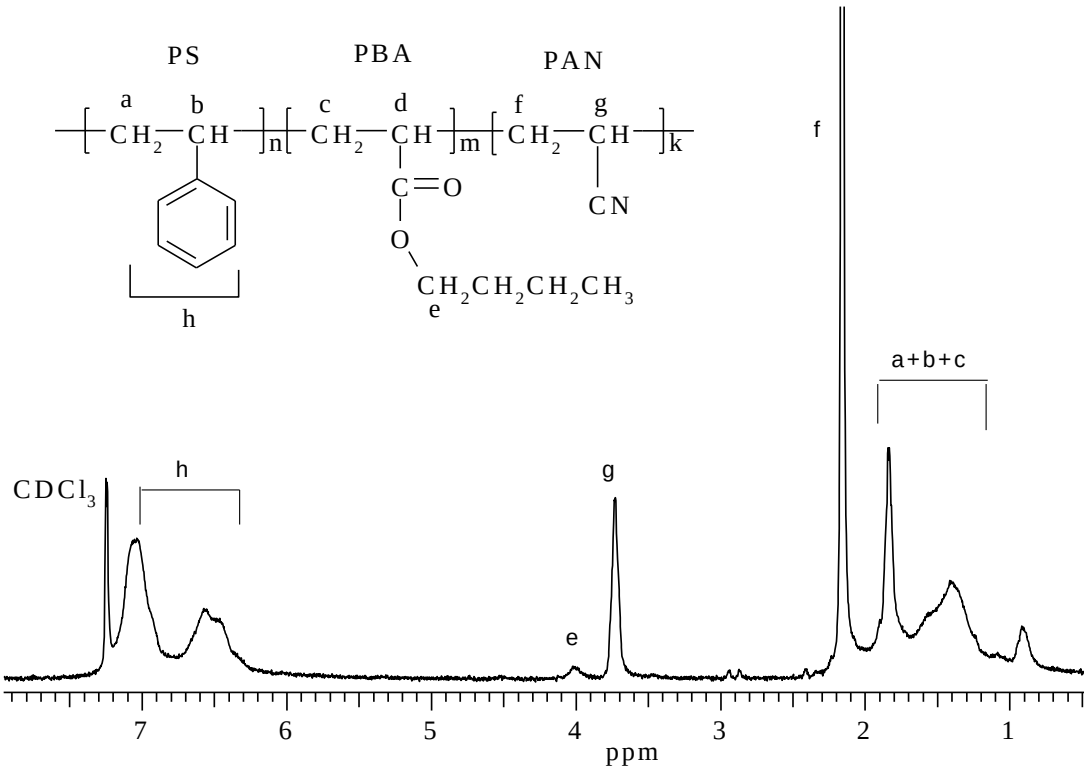


Figure 4.12. ^{1}H-NMR spectrum of PS-*b*-PBA-*b*-PAN in $CDCl_3$ at 25 °C

Table 4.7. Synthesis of PS-*b*-PBA-*b*-PAN by NMP-ATRP-ATRP route.

RUN	Initiator	$[M]_o/[I]_o$	Time (h)	Temp (°C)	Conv (%)	$M_{n,GPC}$[c]	M_{ntheo}	M_n ^{1}H NMR	M_w/M_n	% Composition ^{1}H NMR
IX	1	100	7	125	9	2700	1307	-	1.28	-
X	IX	100	1	70	4	3730	3200	-	1.21	-
XI	X	400	6	70	30	5320	9940	5270	1.11	% 85 PS, % 6 PBA, % 9 PAN
VII	1	100	17	125	49	5670	5550	-	1.23	-
XIII[a]	VII	100	3.5	70	10	7330	6950	8420	1.13	% 72 PS, %28 PBA
X[b]IV	XIII	400	15	70	35	7600	11660	13050	1.16	% 39.7 PS, % 15.7 PBA, % 44.6 PAN

a) $[I]_o/[CuBr]_o/[PMDETA]_o=1/0.5/0.5$

b) $[I]_o/[CuCl]_o/[bpy]_o=1/1/2$

c) The molecular weights were calculated by the aid of linear PS standards.

Table 4.8. Composition of synthesized copolymers and block copolymers calculated by ^{1}H NMR and IR

RUN	Polymer	% PAN by ^{1}H NMR	% PAN by IR	% PS	% PBA
XVII	SAN	17	-	83	-
III	SAN	-	37	63	-
V	SAN-*b*-PS	24	17.7	-	-
XVI	PS-*b*-PAN	37	-	63	-
XIII	PS-*b*-PBA	-	-	68.8	31.2
XV	PS-*b*-PAN	19	-	81	-
XIV	PS-*b*-PBA-*b*-PAN	39	-	27	34

4.6. Analysis of Glass Transition Temperatures

The glass transition temperatures were measured to analyze the phase behavior of synthesized copolymers and block copolymers. The glass transition temperatures of SAN copolymers, SAN-*b*-PS, PS-*b*-PAN and PS-*b*-PBA-*b*-PAN triblock copolymers are collected in Table 4.7. The results obtained indicate that under our experimental conditions one T_g is observed for the case of SAN copolymers and their related block copolymers with PS. Similar results are also observed for PS-*b*-PBA-*b*-PAN triblock copolymers.

Table 4.9. Thermal characterization of copolymers and block copolymers

RUN	Polymer	T_g (°C)
XVII	SAN	92
V	SAN-*b*-PS	98
XVII	PS-*b*-PAN	96
XIII	PS-*b*-PBA	56
XIV	PS-*b*-PBA-*b*-PAN	77

4.7. DSC Diagrams of Block Copolymers

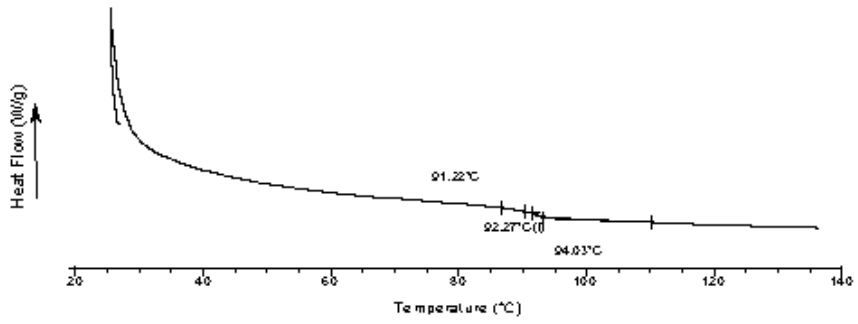


Figure 4.13. DSC thermogram of SAN copolymer

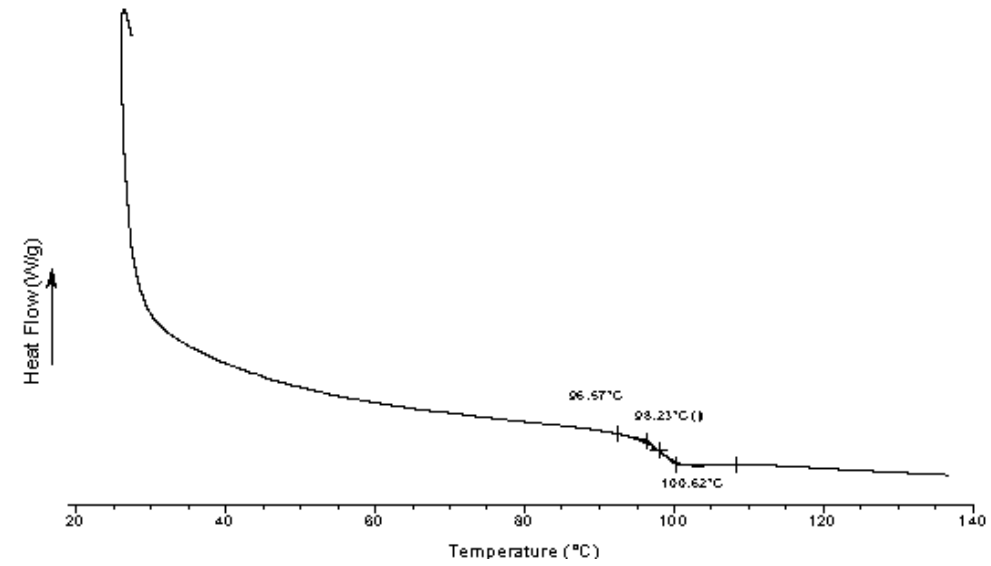


Figure 4.14. DSC thermogram of SAN-*b*-PS

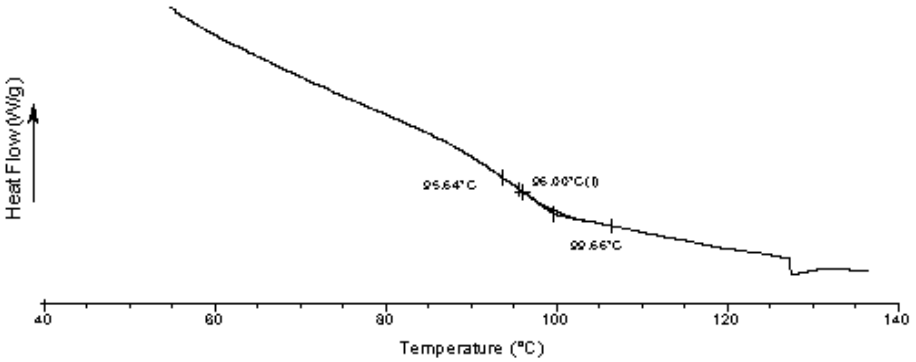


Figure 4.15. DSC thermogram of PS-*b*-PAN.

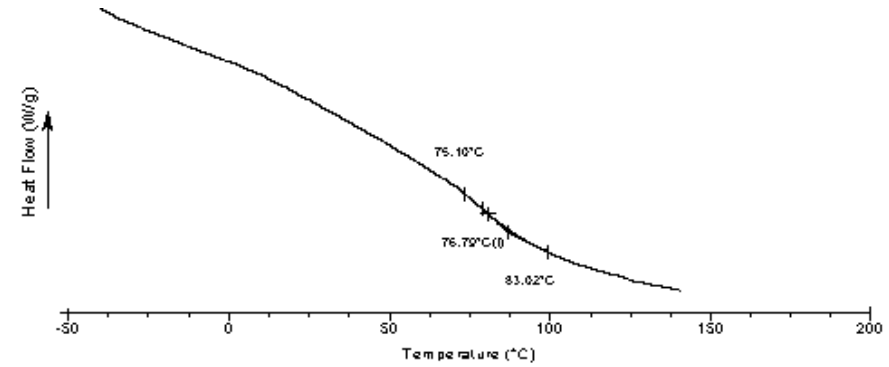


Figure 4.16. DSC thermogram of PS-*b*-PBA-*b*-PAN

Differantial scanning calorimetry (DSC) was used to observe the endothermic and exothermic transitions during the polymerization reaction. The SAN copolymer displayed single transition at 92°C, that is the glass-transition temperature (T_g), the SAN-*b*-PS block copolymer had the characteristic temperatures: T_g = 98°C which

show that SAN copolymers are compatible with linear polystyrene units. The PS-*b*-PAN block copolymer exhibits an endothermic transition at about 96°C. These temperatures were consistent with those of the St and AN blocks [63]. Additionally, the PS-*b*-PBA-*b*-PAN block copolymer displayed one glass transition in the region of 77°C. This transition was almost identical to that of PS and PAN. On the other hand, T_g for the PBA arm was not detected because the PS blocks are longer than the PBA blocks. In this case, the part of the PBA blocks is covered, limiting the movement of the PBA segments. Compared with the confined PBA segments, the PS segments are relatively free so they show a characteristic glass transition [64]. In these thermograms of block copolymers, there was no sign of melting transitions, and these block copolymers were completely resistant toward heating up to 140°C. All DSC scanning was repeated two times to confirm the obtained data. For the study of the thermal behavior of SAN, SAN-*b*-PS, PS-*b*-PAN themselves, samples were equilibrated at 30°C and were heated to 140°C at a heating rate of 10°C/min in a closed cell. However, PS-*b*-PBA-*b*-PAN block copolymer was equilibrated at -70°C and was heated to 140°C at a heating rate of 10°C/min in a closed cell.

4.8. IR Spectra of Synthesized Block Copolymers

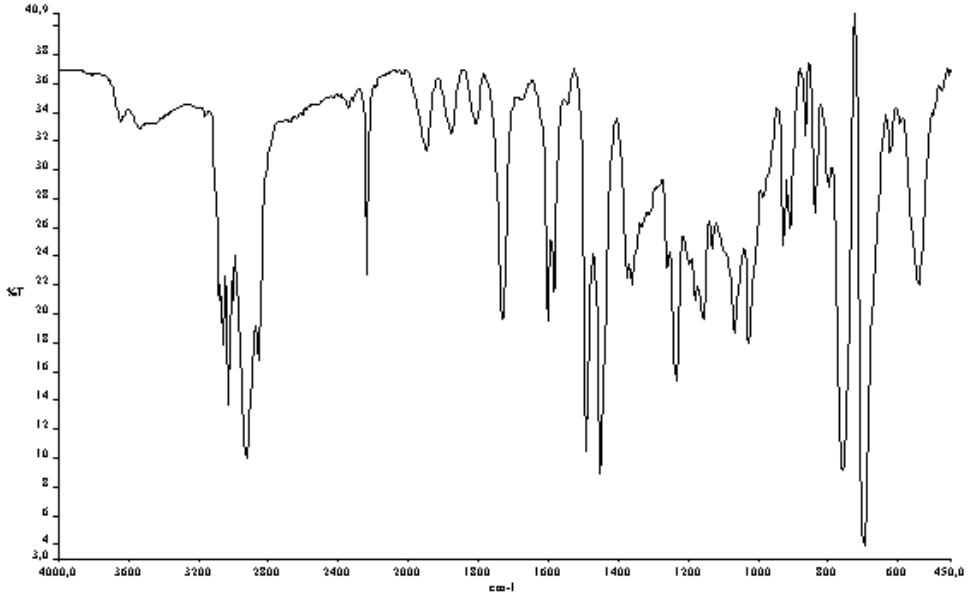


Figure 4.17. IR spectrum of SAN copolymer

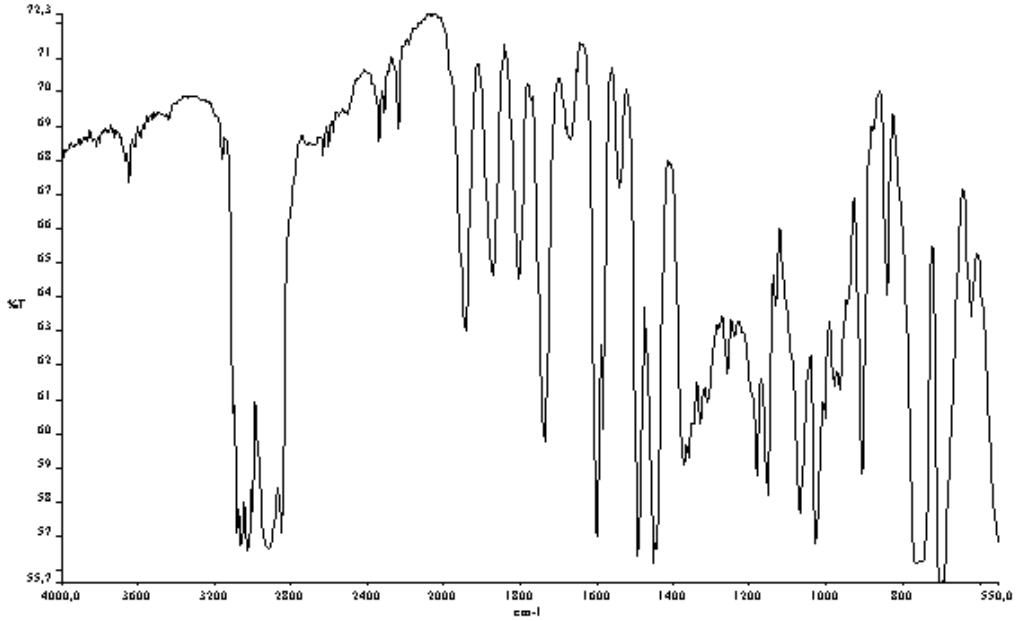


Figure 4.18. IR spectrum of PS-*b*-SAN diblock copolymer.

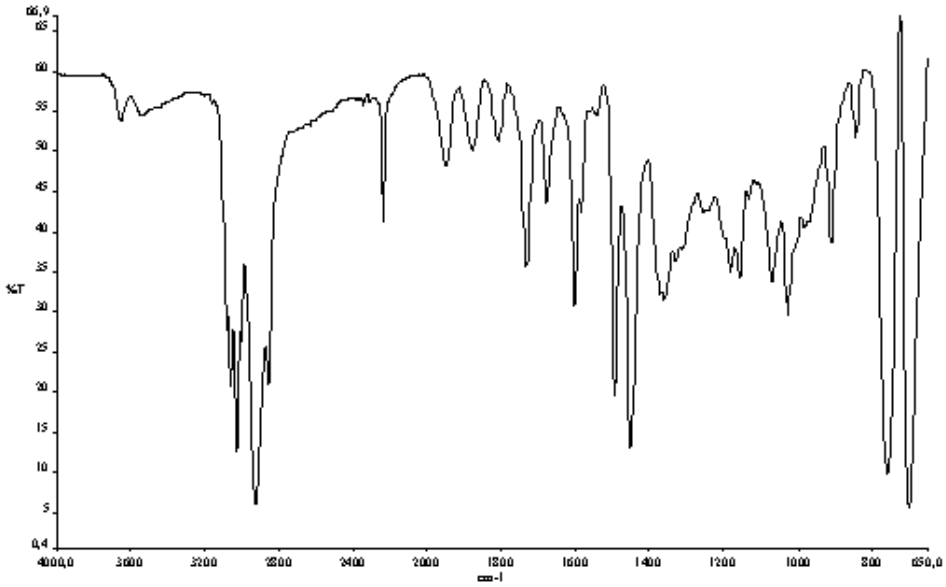


Figure 4.19. IR spectrum of SAN-*b*-PS diblock copolymer.

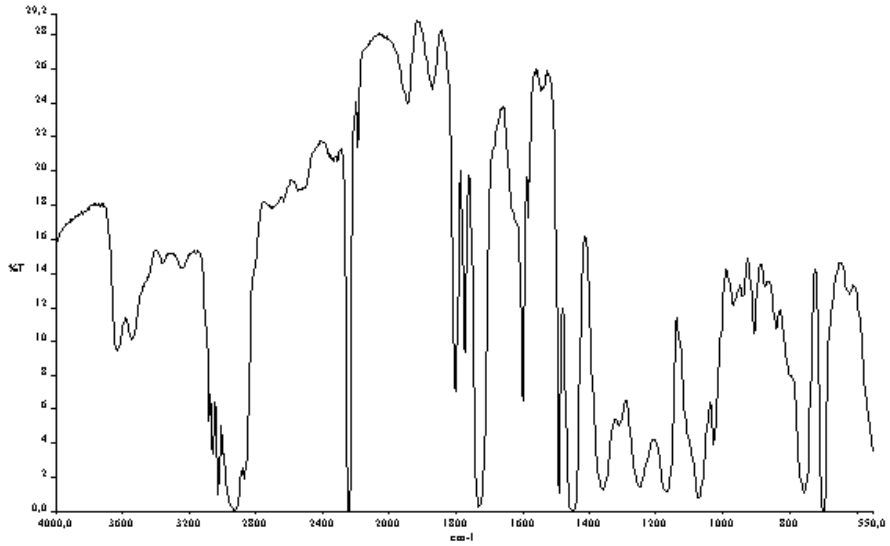


Figure 4.20. IR spectrum of PS-*b*-PBA-*b*-PAN triblock copolymer.

The figures show the IR spectrum of PAN with the prominent nitrile band at 2245 cm^{-1} (-CN stretching vibration). Inclusion of styrene results in a decrease in band intensities of nitrile group at 2245 cm^{-1} and the appearance of bands characteristic of styrene at 700 and 759 cm^{-1} (= CH out-of-plane bending vibration), bands at 1600 and 1459 cm^{-1} (C=C ring stretching vibration) and a band at 3028 cm^{-1} (=C-H stretching vibration). The nitrile group from the AN unit in the (co)polymers is clearly visible. This group absorbs at 2240 cm^{-1}. IR spectrums indicate the complete chemical modification of both polyAN, St/AN copolymer and the block copolymers.

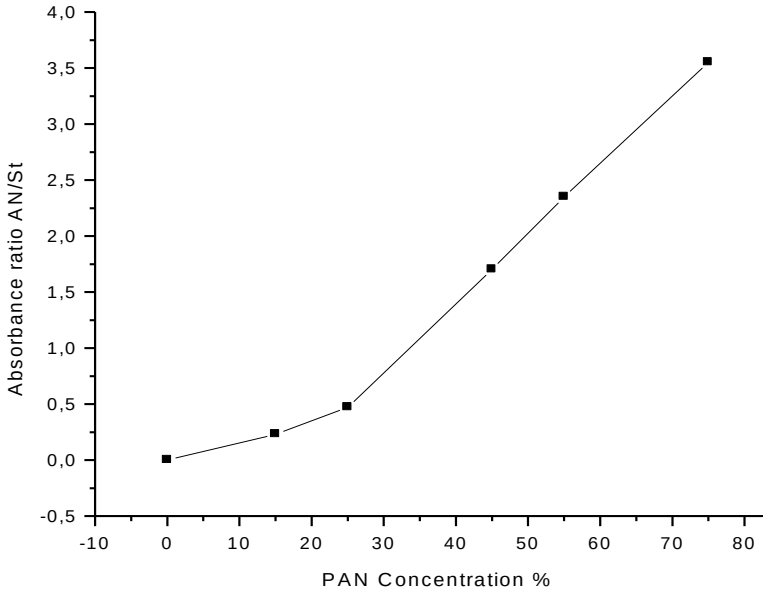


Figure 4.21. Determination of copolymer by FT-IR analysis

A plot of the absorbance ratio as a function of concentration is linear and can be used as a calibration plot. The absorbance ratio for the unknown samples are found and consultation of this graph gives a concentration of AN for the copolymer. Thus, the composition of the copolymers are obtained.

5. CONCLUSION

In conclusion we established a versatile route to the preparation of PAN containing block copolymers using a difunctional initiator 2-phenyl-[2,2,6,6-tetramethylpiperidinooxy]ethyl 2-bromo propionate, (1) combining initiator sites for both NMP and ATRP. We used of difunctional initiator for the synthesis of well-defined SAN copolymers, polystyrene-*block*-polyacrylonitrile (PS-*b*-PAN), polyacrylonitrile-*block*-polystyrene (PAN-*b*-PS), polystyrene-*b*-poly (*n*-butylacrylate)-*b*-polyacrylonitrile (PS-*b*-PBA-*b*-PAN) and also block copolymers containing random SAN sequences and styrene by the combination of ATRP and NMP processes.

The observed molecular weights of homopolymers and block polymers measured by GPC (Gel permeation chromatography) were in reasonably agreement with the theoretical molecular weight and calculated from those of ^{1}HNMR. Block copolymers with various molecular weights and narrow molecular weight distributions were prepared. Furthermore, high end functionality is maintained, making block copolymerization efficient. Well-defined homopolymers, di and triblock copolymers with predetermined block lengths and low polydispersities were synthesized.

These studies are expected to contribute the development of the controlled radical polymerization techniques in a positive way and then enable the manufacturing of the advanced technologic materials with better mechanical and physical properties.

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